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NITRO-*o*-SULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES[1]

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At the time the work upon which this article is based was carried out it was thought desirable to enlarge our knowledge of the substances closely related to *o*-sulphobenzoic acid, which had at that time only recently come into prominence because of its relation to benzoic sulphinide (or saccharin). The immediate object of the investigation was not accomplished and, as the work brought out but little of value, the results have been neglected and allowed to remain unpublished. Since then Taverne[2] has described a few of the compounds first brought to light in the course of this investigation. In some respects his results agree with those of the author. In some respects they do not, as will appear in the course of this article.

Preparation of the Nitro Acid.—One part of the anhydrous *o*-sulphobenzoic acid was weighed into a large beaker glass and two parts of fuming nitric and two parts of pure concentrated sulphuric acid poured over it and the beaker glass gently heated. As soon as the *o*-sulphobenzoic acid had dissolved in the mixed acids a reaction took place, as shown by considerable bubbling and the copious fumes of nitrogen oxides given off. The liquid was heated for some time until all the nitric acid had gone off, the beaker being shaken to facilitate this. After the nitric acid was off the liquid remained quiet, and traces of a crystalline substance began to appear on the sides of the beaker on shaking. The liquid was then cooled down and four or five times its volume of cold water added, when a small quantity of a white crystalline substance appeared, which was immediately filtered off and washed with cold water.

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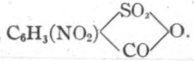
[1] Abstract of a dissertation presented in 1892 to the Board of University Studies of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Rec. trav. chim., **25**, 59 (1906).

When the hot concentrated sulphuric acid solution of the nitro acid is heated a little longer, after the crystalline product appears on the sides of the beaker, there is a sudden change of color from the pale yellow to a dark red, which rapidly becomes darker until a dark reddish brown or almost black, while gases are given off. This secondary action may be due to an action of the sulphuric acid on the nitro acid. It has not been investigated. However this may be, it was thought best not to allow this reaction to take place, as the red coloration produced was very hard to get rid of and the salts prepared from such an acid were less pure.



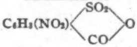
Anhydride of Nitro-o-sulphobenzoic Acid, $C_6H_3(NO_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle O$. —This is the white crystalline substance which separated from the concentrated sulphuric acid solution on addition of cold water. It was dried between filter papers over sulphuric acid to prepare it for analysis. It was found to melt at about 212° (uncorrected).

In the analyses the carbon was determined by combustion in an open tube with lead chromate in a stream of oxygen. The sulphur was determined by Liebig's method and the nitrogen by Gunning's modification of Kjeldahl's method.

I. 0.34095 gram substance gave 0.35475 gram $BaSO_4$.
II. 0.2592 gram substance gave 0.26149 gram $BaSO_4$.
III. 0.6399 gram substance gave 0.03763 gram N.
IV. 0.46175 gram substance gave 0.02764 gram N.
V. 0.5403 gram substance gave 0.03478 gram N.

VI. 0.1570 gram substance gave 0.21021 gram CO_2 and 0.0340 gram H_2O.

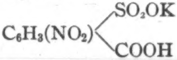
VII. 0.1579 gram substance gave 0.2151 gram CO_2.



	Calculated for $C_6H_3(NO_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle O$	Found						
		I	II	III	IV	V	VI	VII
S	13.97	14.30	13.86	....	....	....	...	...
N	6.11	...	...	5.86	5.98	6.43	...	...
C_7	36.67	...	...	....	....	....	36.51	37.13
H_3	1.31	...	...	....	....	....	2.14	...

The anhydride dissolves in cold water slowly, but easily in hot water or alcohol, forming the acid.

Taverne[1] nitrated the three sulphobenzoic acids by treating 1 gram of each of the anhydrous acids with 5 to 6 grams of nitric acid and, after solution had been effected, removing the nitric acid *in vacuo* over potassium hydroxide. In the case of the ortho acid a syrupy mass was obtained which, on standing *in vacuo* over sulphuric acid, began to crystallize and, at the end of two days, had been transformed into a porcelainlike mass which softened at about 90° and melted completely at 144°. He did not obtain the anhydride.

Acid Potassium Salt,  $C_6H_3(NO_2)\left\langle\begin{matrix}SO_2OK\\COOH\end{matrix}\right.$ + H_2O.—The filtrate from the anhydride, consisting of the nitro acid and sulphuric acid, was diluted, and the sulphuric acid removed by means of calcium carbonate. The solution of the calcium salt thus obtained was then treated with potassium carbonate. The solution of the potassium salt was made strongly acid with hydrochloric acid and evaporated to crystallization. On cooling, the acid potassium salt separated out in fine yellow needles and tufts. These were separated from the mother liquor, boiled with animal charcoal and recrystallized, when the salt came out again as fine yellow needles, accompanied by a much smaller quantity of stout prisms and plates, apparently of the triclinic system and much resembling axinite. Some of the prisms were mechanically separated from the needles, dissolved in water and allowed slowly to crystallize over sulphuric acid, when a group of prisms was obtained. These were afterwards obtained in needles.

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[1] *Loc. cit.*

The purified salt, containing both kinds of crystals, was analyzed and found to contain one molecule of water of crystallization.

I. 0.18675 gram salt gave 0.0531 gram K_2SO_4.
II. 0.1500 gram salt gave 0.0430 gram K_2SO_4.
III. 0.15085 gram salt lost (at 140°) 0.0089 gram H_2O.
IV. 0.5456 gram salt lost (at 140°) 0.0327 gram H_2O.
V. 0.1989 gram salt gave 0.1477 gram $BaSO_4$.

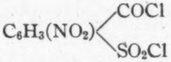
	Calculated for $C_6H_3(NO_2)\left\langle\begin{matrix}COOH\\SO_3K\end{matrix}\right. + H_2O$	Found				
		I	II	III	IV	V
K	12.87	12.76	12.84	....	....	...
H_2O	5.93	...	...	5.89	5.99	...
S	10.56	...	...	....	....	10.21

The analysis seems to show that the salt is pure, though, as the difference in crystallization would indicate, there may be an isomeric product present containing the same water of crystallization.

Chlorides of Nitro-o-sulphobenzoic Acid.—The acid potassium salt was dried, finely pulverized and mixed in an Erlenmeyer flask with a double quantity of phosphorus pentachloride. After the reaction had taken place the flask and contents were heated in a sulphuric acid bath to 120° until the oxychloride seemed to be off, then allowed to cool and washed repeatedly with large volumes of cold water until the washings were no longer turbid. The chloride was thus obtained as a light yellow oily-looking liquid, and was usually accompanied by a small amount of a white granular substance.

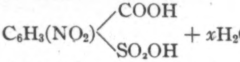
In two preparations of the chloride, when it was desirable to have it free from water, the wash water was poured off as much as possible and the chloride extracted from the remainder with ether. When the ether was distilled off the chloride remained behind as a reddish oil. The white granular substance was found to be insoluble in ether and was filtered off. It is insoluble in cold water, but dissolves on boiling, the solution giving a test for hydrochloric acid. When the solution is evaporated nearly to dryness small clusters of needlelike crystals of an acid are deposited. The small quantity of this substance obtained prevented any further investigation.

The nitro-*o*-sulphobenzoic dichloride was found to be insoluble in benzene and petroleum ether, but soluble in ordinary ether. It dissolves in boiling water with formation of the acid, and in cold alcohol with formation of the chloride ester, which is converted by water into the acid ester. With concentrated ammonia water or gaseous ammonia it reacts to form the sulphinide. Its constitution is shown by its reactions and mode of preparation to be.



$$C_6H_3(NO_2)\begin{cases}COCl\\SO_2Cl\end{cases}$$

An attempt was made to purify it by crystallization from ether at a low temperature, but without a satisfactory result. The chloride forms a viscous mass at —10°.



Nitro-o-sulphobenzoic Acid, $C_6H_3(NO_2)\begin{cases}COOH\\SO_2OH\end{cases} + xH_2O$.— The chloride was boiled with water until all had gone into solution, then boiled with animal charcoal, filtered and the filtrate evaporated to a syrup. Nothing crystallized out of this on standing exposed to the air. On standing over sulphuric acid for a long time small prisms crystallized out, but in insufficient quantity for an analysis. The very concentrated solution of the acid, when heated to a high temperature, turns dark and fumes with an odor like burnt sugar. The concentrated solution attacks organic matter, such as filter paper, very much as sulphuric acid or a concentrated solution of *o*-sulphobenzoic acid does. The anhydride also shows this property when heated to 90°. From the solution of the acid a series of salts was made.

Taverne[1] describes the free acid as being easily soluble in water and alcohol, very slightly in ether, insoluble in benzene, petroleum ether and chloroform. According to him it separates with 2 molecules of water and melts at 105° when dried in a desiccator.

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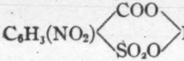
[1] *Loc. cit.*

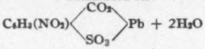
Lead Salt of Nitro-o-sulphobenzoic Acid,



$C_6H_3(NO_2)\left<\begin{matrix}COO\\SO_2O\end{matrix}\right>Pb + 2H_2O$.—This was prepared by boiling a solution of the acid with pure precipitated lead carbonate, filtering and evaporating the solution until a slight scum was formed on the sides of the vessel. The lead salt separated out in small acicular crystals containing two molecules of water of crystallization and easily soluble.

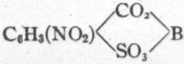
I. 0.2161 gram salt lost (at 160°) 0.0151 gram H_2O.

II. 0.1249 gram salt lost (at 160°) 0.0090 gram H_2O.

	Calculated for  $C_6H_3(NO_2)\left<\begin{matrix}CO_2\\SO_3\end{matrix}\right>Pb + 2H_2O$	Found I	 II
$2H_2O$	7.37	6.99	7.20

On evaporating the solution of the salt down to a small volume another lead salt separated out as a crust on the sides and bottom of the vessel. It was much more difficultly soluble than the crystallized salt and was apparently basic, as when dried at 100° and then heated to 140° it lost a little less than a molecule of water. No satisfactory analysis of this was obtained.

Barium Salt of Nitro-o-sulphobenzoic Acid,



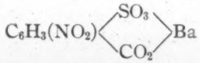
$C_6H_3(NO_2)\left<\begin{matrix}CO_2\\SO_3\end{matrix}\right>Ba + 3H_2O$.—This was prepared like the lead salt by boiling a dilute solution of the free acid with pure barium carbonate, filtering and evaporating the solution of the barium salt until a slight scum appeared. On standing several hours a moderate quantity of needlelike crystals appeared. These were recrystallized, dried and analyzed. They were found to contain three molecules of water of crystallization, all of which was lost by heating to 160°. The salt is not very easily soluble in water.

I. 0.2524 gram salt gave 0.1340 gram $BaSO_4$, and lost 0.0315 gram H_2O.

II. 0.3054 gram salt gave 0.15925 gram $BaSO_4$, and lost 0.0385 gram H_2O.

	Calculated fo $C_6H_3(NO_2)\left\langle\begin{matrix}SO_3\\CO_2\end{matrix}\right\rangle Ba + 3H_2O$	Found I	II
Ba	31.42	31.22	30.66
$3H_2O$	12.67	12.57	12.66

On evaporating the solution of this salt down to a small volume the salt separated out in small flakes over the bottom of the beaker. It was filtered off and dried between filter papers. On analysis it was found to be the anhydrous barium salt:



$$C_6H_3(NO_2)\left\langle\begin{matrix}SO_3\\CO_2\end{matrix}\right\rangle Ba$$

Taverne's[1] description of the barium salt obtained by him agrees with the above except that he says it is necessary to heat the salt to 200° to drive off all the water of crystallization.

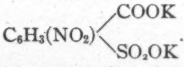
I. 0.3058 gram salt gave 0.1854 gram $BaSO_4$.

II. 0.3602 gram salt gave 0.2208 gram $BaSO_4$.

	Calculated for $C_6H_3(NO_2)\left\langle\begin{matrix}CO_2\\SO_3\end{matrix}\right\rangle Ba$	Found I	II
Ba	35.88	35.66	36.05

It was found to be much more difficultly soluble than the crystallized salt.

Neutral Potassium Salt of Nitro-o-sulphobenzoic Acid,



$C_6H_3(NO_2)\left\langle\begin{matrix}COOK\\SO_2OK\end{matrix}\right.$.—This was prepared by exactly neutralizing a solution of the acid salt with a dilute solution of potassium carbonate, filtering and evaporating until the salt separated. No crystals of this salt were obtained. The salt thus prepared contains no water of crystallization. It was dried at 100° and analyzed.

I. 0.3079 gram salt gave 0.1665 gram K_2SO_4.

II. 0.3627 gram salt gave 0.1951 gram K_2SO_4.

	Calculated for $C_6H_3(NO_2)\left\langle\begin{matrix}CO_2K\\SO_3K\end{matrix}\right.$	Found I	II
K_2	24.14	24.27	24.16

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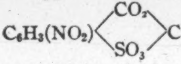
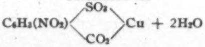
[1] *Loc. cit.*

Copper Salt of Nitro-o-sulphobenzoic Acid,



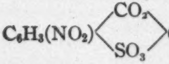
$C_6H_3(NO_2)\left<\begin{matrix}CO_2\\SO_3\end{matrix}\right>Cu + 2H_2O$.—This was prepared by exactly precipitating the barium salt by a dilute solution of pure copper sulphate and filtering off the barium sulphate. The pale green solution of the copper salt so obtained was evaporated, first on an asbestos board and finally on a water bath kept at 70°. It was found that if the evaporation of the solution went on too rapidly a pale blue basic salt separated out which was difficultly soluble in water. The solution of the salt when brought down to a very concentrated solution deposited a fibrous crystalline mass of the copper salt. This was freed from the mother liquor as much as possible by the filter pump and then spread over an unglazed porcelain plate and kept over sulphuric acid for a couple of weeks, when the coating of salt became quite hard. It was scraped off, pulverized, and dried in an air bath at 70°, and again kept over sulphuric acid until the pale green powder began to whiten at the edges. It was then analyzed for water of crystallization. It was found to contain two molecules of water, like the lead salt, which it lost at 160°–170°.

I. 0.3463 gram salt lost 0.0363 gram H_2O.
II. 0.3543 gram salt lost 0.0375 gram H_2O.

	Calculated for  $C_6H_3(NO_2)\left<\begin{matrix}SO_3\\CO_2\end{matrix}\right>Cu + 2H_2O$	Found I	 II
$2H_2O$	10.46	10.48	10.58

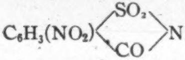
The anhydrous salt is brown and when treated with water becomes green, but is difficultly soluble.

Calcium Salt of Nitro-o-sulphobenzoic Acid,

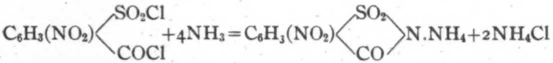


$C_6H_3(NO_2)\left<\begin{matrix}CO_2\\SO_3\end{matrix}\right>Ca + xH_2O$.—This salt was prepared by boiling the free acid with pure precipitated calcium carbonate, filtering and evaporating to crystallization. It separates from a not too concentrated solution in fine short needles much resembling the barium salt.

Sulphinide of Nitro-o-sulphobenzoic Acid,



$C_6H_3(NO_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle NH$.—This was prepared from the dichloride of the acid by treatment with dry ammonia. The reaction is represented thus:

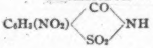


$$C_6H_3(NO_2)\left\langle\begin{matrix}SO_2Cl\\COCl\end{matrix}\right. + 4NH_3 = C_6H_3(NO_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle N.NH_4 + 2NH_4Cl$$

Two ways were tried to effect this reaction. The first was to pass dry ammonia gas over the chloride in a liquid or viscous state, stirring frequently to expose a fresh surface to the ammonia. After the experiment had proceeded as long as was deemed necessary the solid mixture of chloride and sulphinide was treated with water and the dissolved ammonium salts poured off from the unchanged chloride. Hydrochloric acid was then added to the solution, which was evaporated to a small volume, when part of the sulphinide separated out. This was recrystallized several times, but still contained considerable ammonium chloride, as the sulphinide is nearly as soluble as this salt. It is more soluble in alcohol than ammonium chloride, and this fact was also used for its purification.

A second method was found to give a much larger yield of the ammonium salt of the sulphinide. The dichloride was dissolved in ether and a rapid stream of ammonia passed into the solution. The ammonium salts were precipitated as a dirty yellow granular mass. This was filtered off and washed with ether. It consisted of the ammonium salt of the sulphinide with ammonium chloride, most of which was gotten rid of by repeated crystallization. The lead salt was made by boiling with lead oxide, filtering and evaporating to a small volume, when it separated on cooling. It was again dissolved and the lead exactly precipitated by dilute sulphuric acid, leaving the free sulphinide in solution. An attempt was made to crystallize it from water, but, as it is quite soluble, no great success was reached. It is less soluble in alcohol, and a small amount, about 0.250 gram, was obtained from a concentrated alcoholic solution. There was probably a little ammonium chloride still present, which would account for the high results in the determination of nitrogen.

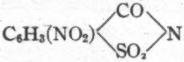
I. 0.2780 gram sulphinide gave 0.040216 gram N.
II. 0.2358 gram sulphinide gave 0.033016 gram N.

	Calculated for	Found	
	 $C_6H_3(NO_2)\left<\begin{matrix}CO\\SO_2\end{matrix}\right>NH$	I	II
N_2	12.28	14.45	13.53

It was also attempted to prepare the sulphinide by passing dry ammonia gas into the anhydride suspended in ether, but without success.

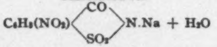
Nitrobenzoic sulphinide is very soluble in water, less soluble in alcohol and insoluble in ether. It possesses an intensely bitter taste, greatly resembling quinine, but with a slightly sweet after-taste. It resembles in this respect *p*-nitrobenzoic sulphinide prepared by Noyes[1] from *p*-nitro-*o*-toluenesulphonamide, but differs from it in being more easily soluble.

Sodium Salt of the Nitrosulphinide,



$C_6H_3(NO_2)\left<\begin{matrix}CO\\SO_2\end{matrix}\right>N.Na + H_2O$.—This was prepared by adding an excess of sodium hydroxide to a solution of the ammonium salt together with ammonium chloride and boiling off all the ammonia. It was then carefully neutralized with hydrochloric acid and evaporated to dryness, powdered and extracted with alcohol. After the alcohol had been distilled off the extract was dissolved in water and recrystallized several times until a small quantity of the needlelike crystals of the sodium salt was obtained. These contain one molecule of water of crystallization.

I. 0.2477 gram salt lost (at 150°) 0.0177 gram H_2O.
II. 0.1799 gram salt lost (at 150°) 0.0128 gram H_2O.

	Calculated for	Found	
	 $C_6H_3(NO_2)\left<\begin{matrix}CO\\SO_2\end{matrix}\right>N.Na + H_2O$	I	II
H_2O	7.08	7.18	7.11

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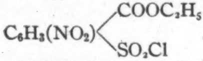
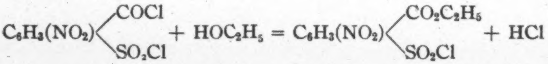
[1] This Journal, 8, 170.

This salt is quite soluble in water, less so in alcohol. It has not the extremely bitter taste of the ammonium salt and the sulphinide, but is rather sweet with a slight bitterness.

Ethyl Ester Chloride of Nitro-o-sulphobenzoic Acid,

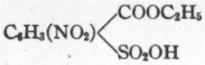


$C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_2H_5\\SO_2Cl\end{array}\right.$.—This was prepared by treating the chloride with cold strong alcohol and evaporating off the excess of alcohol. It forms an oily liquid. The reaction is represented thus:

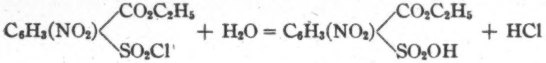


$$C_6H_3(NO_2)\left\langle\begin{array}{l}COCl\\SO_2Cl\end{array}\right. + HOC_2H_5 = C_6H_3(NO_2)\left\langle\begin{array}{l}CO_2C_2H_5\\SO_2Cl\end{array}\right. + HCl$$

When dissolved in hot water it formed the acid ethyl ester:



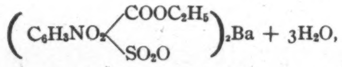
$$C_6H_3(NO_2)\left\langle\begin{array}{l}COOC_2H_5\\SO_2OH\end{array}\right.$$



$$C_6H_3(NO_2)\left\langle\begin{array}{l}CO_2C_2H_5\\SO_2Cl\end{array}\right. + H_2O = C_6H_3(NO_2)\left\langle\begin{array}{l}CO_2C_2H_5\\SO_2OH\end{array}\right. + HCl$$

From this was made, by neutralizing with barium carbonate,

Barium Ethyl Nitro-o-sulphobenzoate,



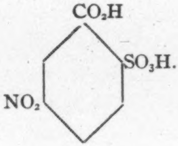
$$\left(C_6H_3NO_2\left\langle\begin{array}{l}COOC_2H_5\\SO_2O\end{array}\right.\right)_2Ba + 3H_2O,$$

crystallizing in colorless needles containing three molecules of water of crystallization.

I. 0.1397 gram salt lost (at 145°) 0.0100 gram H_2O.
II. 0.1663 gram salt lost (at 145°) 0.0121 gram H_2O.
III. 0.0208 gram salt gave 0.0071 gram $BaSO_4$.

	Calculated for $\left(C_6H_3(NO_2)\left\langle\begin{array}{l}CO_2C_2H_5\\SO_2O\end{array}\right.\right)_2Ba + 3H_2O$	Found I	II	III
$3H_2O$	7.30	7.16	7.27	...
Ba	18.54	....	....	19.87

An attempt was made to determine the position of the nitro group in the nitro acid by preparing the corresponding amino acid, diazotizing, and decomposing the diazo compound by boiling with water. This was not successful, though the results obtained made it appear probable that the nitro group is situated para to the sulpho group, and meta to the carboxyl. Taverne[1] has since shown that this view of the constitution of the acid is correct. He heated the anhydrous nitration product with phosphorus pentachloride up to about 180°, then boiled with water, when he obtained 2-chloro-5-nitrobenzoic acid, showing that the principal product of the nitration of *o*-sulphobenzoic acid is the nitro acid having the nitro group in the position represented in the formula



THE OXIDATION OF NITROGEN AND OXYGEN

By W. W. Strong

One of the most important problems in the chemistry of gas reactions is that of determining the exact mechanism of the reactions. What reactions are involved in the production of O_3; of NO?

Quite recently, R. J. Strutt[2] and his coworkers have published a series of papers on the reactions in which nitrogen is involved. Strutt's method consists in producing modifications of various substances in the electrical discharge and carrying these out of the region of the discharge ("afterglows") and then studying the chemical properties of the modified substances. During many of these reactions various characteristic spectra are emitted and it was hoped that the carriers of these spectra could be determined so that it would be possible to know the nature of the chemical reactions taking place in the various regions of arc and spark discharges through the nature of the light emitted.

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[1] *Loc. cit.*

[2] P. Physic. Soc., **1910**, 66; **1911**, 147. P. Roy. Soc., **85A**, 219 (1911). Fowler and Strutt: *Ibid.*, **85**, 377 (1911); **86**, 56 (1911). See This Journal, **50**, 100.

Following are some characteristics of afterglows and different kinds of flames. The afterglows result from electrical discharge in vacuum tubes:

Pure oxygen	Weak afterglow
Air	Bright yellow; moisture has little effect
Pure nitrogen	None
Pure nitrogen	Glows when there is a spark discharge with capacity
Ozonized oxygen on H_2S or CS_2	Sky-blue flame possessing bands between λ2600 and λ2300
Ozonized oxygen on SO_2 or Sb or H_2, or CO or NH_3	No glow
Ozonized oxygen on acetylene	Swan spectrum
Ozonized oxygen on benzene	Weak glow
Ozonized oxygen on cyanogen	White glow
Nitrogen glow on mercury	Explosive compound
Nitrogen glow on acetylene	Cyanogen formed
Nitrogen glow on oxygen	Glow destroyed
Nitrogen glow on hydrogen	No effect
Nitrogen glow on nitric oxide	Greenish yellow flame giving the peroxide. The amount of this oxidation is taken as the measure of the amount of the glow

On account of the failure to liquefy the active modification of nitrogen, Strutt has assumed it to be a monatomic form of that element. It will therefore be designated by N.

The afterglow in air is considered as being probably due to the oxidation of nitric oxide by ozone, this being a kind of phosphorescent combustion. The nitrogen afterglow is not charged; is weakened by heating and intensified by cooling. The "yellowish green" flame characteristic of the high tension arc appears to be due to oxidation of oxides of nitrogen by ozone. This type of reaction may take place when:

(1) Ozone is mixed with NO or N_2O_2
(2) Ozone is mixed with NO_2 or N_2O_4
(3) N is mixed with NO or NO_2
(4) NO is fed into a Bunsen flame
(5) NO_2 is fed into a Bunsen flame

In the work of J. J. Thomson on positive rays the following kinds of ions have been detected: .

$$\overset{-}{O_2};\ \overset{-}{O};\ \overset{+}{O};\ \overset{+}{O_3};\ \overset{+}{O_6};\ \overset{++}{O}$$

$$\overset{++}{N};\ \overset{+}{N};\ \overset{+}{N_2};\ \overset{+}{N_3};\ \overset{+++}{N}$$

Assuming that dissociation takes place, we have O and N as well as O_2, N_2 and O_3, all these being neutral. If, then, the above are the only states of existence of oxygen and nitrogen matter, ozone and nitric oxide must be formed from one or more of the above products. The formation of ozone might take place in the following manner, *e* representing an electron:

$$(1)\ \overset{-}{O_2} + \overset{-}{O} = O_3 - 2e$$

$$(2)\ \overset{-}{O_2} + \overset{+}{O} = O_3$$

$$(3)\ \overset{-}{O_2} + \overset{++}{O} = O_3 + e$$

$$(4)\ \overset{-}{O} + \overset{-}{O} + \overset{-}{O} = O_3 - 3e$$

$$(5)\ \overset{-}{O} + \overset{-}{O} + \overset{+}{O} = O_3 - e$$

$$(6)\ \overset{-}{O} + \overset{+}{O} + \overset{+}{O} = O_3 + e$$

$$(7)\ \overset{-}{O} + \overset{++}{O} + \overset{++}{O} = O_3 + 3e$$

$$(8)\ \overset{-}{O} + \overset{-}{O} + \overset{++}{O} = O_3$$

$$(9)\ \overset{-}{O} + \overset{+}{O} + \overset{++}{O} = O_3 + 2e$$

$$(10)\ \overset{+}{O} + \overset{+}{O} + \overset{+}{O} = O_3 + 3e$$

$$(11)\ \overset{+}{O_6} = 2O_3 - e$$

$$(12)\ O + O + O = O_3$$

$$(13)\ \overset{+}{O} + \overset{-}{O} + O = O_3$$

$$(14)\ \overset{-}{O_2} + O = O_3 - e, \text{ etc.}$$

These are not all the possible equations representing what may take place. By assuming a certain distribution of each one of these "products," a certain distribution of velocities and of electrostatic charge, it would probably be possible to calculate the relative probabilities of each one of these reactions taking place. Naturally, other things being equal, the probability will be greatest for those equations containing positive and negative products. The most efficient method of producing ozone will be based upon the equation possessing the greatest probability of occurrence. At the present time we have no idea what the equation for the formation of ozone really is.

The electrical method promises to be of very great service in answering this problem, provided the reactions are carried on for comparatively large mean free paths.

The formation of nitric oxide can be an equally complex process.

(1) $\overset{-}{O_2} + \overset{++}{N} = NO + e + O$
(2) $\overset{-}{O_2} + \overset{+}{N} = NO + O$
(3) $\overset{-}{O_2} + \overset{+}{N_2} = 2NO$
(4) $\overset{-}{O_2} + \overset{+}{N_3} = 2NO + N$
(5) $\overset{-}{O_2} + \overset{+++}{N} = NO + 2e + O$
(6) $\overset{-}{O} + \overset{+}{N} = NO$
(7) $\overset{-}{O} + \overset{+}{N_2} = NO + N$
(8) $O + N = NO$
(9) $\overset{+}{O_3} + \overset{+}{N_3} = 3NO + 2e$
(10) $\overset{+}{O} + N = NO + e$, etc., etc.

It is seen that the formation of nitric oxide may be even more complex than the formation of ozone. Let us assume that the resultant product is formed by the combination of two "products" into a neutral molecule. The possible equations are then as follows:

(1) $\overset{-}{O_2} + \overset{+}{O} = O_3$
(2) $3O = O_3$
(3) $O + O_2 = O_3$
(4) $\overset{-}{O} + \overset{+}{O} + O = O_3$
(5) $\overset{-}{O} + \overset{-}{O} + \overset{++}{O} = O_3$

(1) $O + N = NO$
(2) $O_2 + N_2 = 2NO$
(3) $O + N_2 = NO + N$
(4) $O_2 + N = NO + O$
(5) $\overset{-}{O_2} + \overset{+}{N} = NO + O$
(6) $\overset{-}{O_2} + \overset{+}{N_2} = 2NO$
(7) $\overset{-}{O_2} + \overset{+}{N_3} = 2NO + N$
(8) $\overset{-}{O} + \overset{+}{N} = NO$
(9) $\overset{-}{O} + \overset{+}{N_2} = NO + N$
(10) $\overset{-}{O} + \overset{+}{N_3} = NO + N_2$

If the process is electrical, that is, if an intense state of ionization is necessary in order that the reaction take place, then only those reactions that are italicized would be possible. The relative intensity of the various "products" in the positive rays might be taken as indicating the relative probability of the occurrence of these reactions. Since rays of $\overset{-}{O}$ and $\overset{-}{O_2}$ are quite bright and since it is very unlikely that the products should collide simultaneously, we may conclude that ozone is formed by the following reaction:

$$\overset{-}{O_2} + \overset{+}{O} = O_3$$

Since the concentration of dissociated products must be very small, the formation of nitric oxide probably takes place according to the following equations, the pressure and temperature being the main determining factors:

$$\overset{-}{O_2} + \overset{+}{N} = NO + O$$

$$\overset{-}{O_2} + \overset{+}{N_2} = 2NO$$

$$\overset{-}{O} + \overset{+}{N_2} = NO + N$$

At atmospheric pressure it is probable that the reaction is mainly:

$$\overset{-}{O_2} + \overset{+}{N_2} = 2NO$$

This conclusion is in agreement with Strutt's result that active nitrogen did not seem to be necessary for the production of nitric oxide.

It was thought that possibly the use of a corona discharge might indicate something concerning the nature of the reactions involved in the production of nitric oxide. Corona discharges may consist of streams of positive ions, of negative ions or of both positive and negative ions. A typical form of corona discharge is that between wires *F*, and cylinders *P*, as indicated in Fig. I. Either the active (wires where the electric field is very intense) or the passive electrodes (where the electric field is comparatively weak) may be grounded. By grounding the "active" electrode and passing a low voltage

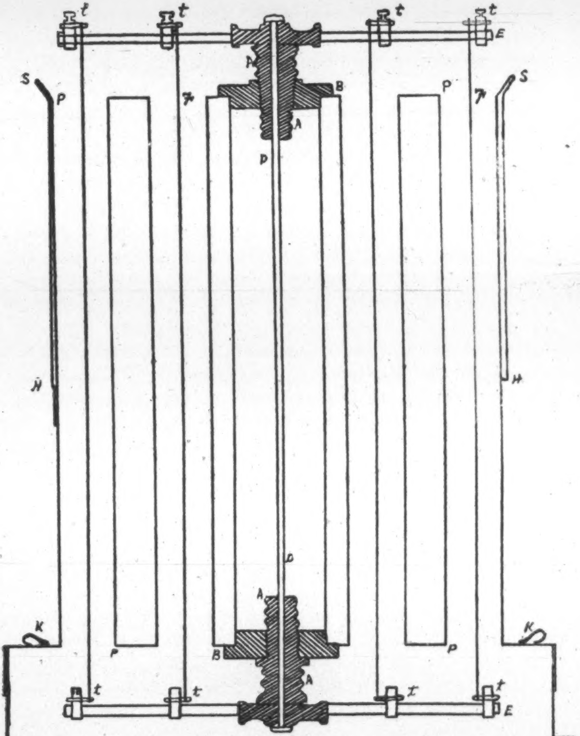

Fig. I

current through it, the temperature can be given any desired value. By using a suction fan, gases can be drawn through *F* and *O* through an absorbing solution of hydroxide. Sodium hydroxide (1.042 normal) was used in some of the experiments. By making the active electrodes porous the ions could be made either of oxygen or nitrogen. The particular electrodes of Fig. I consisted of No. 20 English gauge wire in 5-inch cylinders. The corona discharge could be made either positive or negative.

The corona discharge does not resemble any of the flames described above, so that it is at present impossible to get any clue as to what regions ozone and nitric oxide are being formed in. Following is a description of the positive and negative coronas. The alternating corona is a combination of both. The two photographs (Figs. II and III) were taken at the same voltage.[1]

In air the positive corona consists of fine branching, bluish purple brushes darting a cm. or more from the wire. When the ionic current density is great enough there is a thin, bluish purple film covering the wire. This is accompanied by a slight buzzing noise. The positive corona is not greatly affected by the presence of dirt. The brush discharge consists of straight stems of considerable luminosity, from which dart forth twiglike, purplish violet branches. The pitch of the hissing sound produced depends on the proximity of neighboring conductors.

Viewing a precipitation chamber with 30 or more wires axially placed within earthed cylinders gives a wavy, luminous effect somewhat like the northern lights effect. If the wire is not exactly concentric to the cylinder, the brush and branches swing to the region where the electric field is most intense. Looking at the cylinder end on gives one the impression that the whole region between the wire and the nearest side of the cylinder is filled with luminosity, though it is doubtful if this is the case. When this condition is reached and the voltage fluctuates slightly, occasional oscillatory sparks will take place. When a wire is more than 6 mm. in diameter only disruptive discharges occur.

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[1] For the electrical connections see P. Am. Inst. Elec. Eng., p. 1303, June, 1913.

In the case of a "dirty" wire several brushes will discharge per cm. length of wire, the intensity of the brushes constantly varying. Each brush starts from a bright point on the wire, the brightness of the point increasing with the size of the brush. Numerous points of less brightness also appear between the main brush points, the discharge from these points being too weak to give visible brushes.

The accompanying Fig. II is a photograph of the positive corona taken with the camera focused upon the end of the precipitation chamber represented in a later photograph. The lowest wire near the middle of the picture is the best focused and shows very clearly the stems and twiglike, purplish violet branches. The wire on the left side of the photograph is out of focus. Smoke and dust can easily pass through the purplish violet branch discharges. With the exception of the points at which these brush discharges originate, the wires show very little luminosity.

The negative corona consists of bright, stationary, reddish discharges from 3 to 5 mm. in length. No bright film is present. A loud buzzing noise is produced. The negative brush is but slightly influenced by the presence of surrounding conductors. Dirt decreases the noise and causes the discharge to become more localized and to start at a much lower voltage. On the wires of a precipitation chamber the negative corona fills only a comparatively small region of the cylinder and slight variation of the position of the wire from the axial position does not distort the radial symmetry of the discharge about the wire. The number of bright points on the wire is much larger than in the case of the positive corona. The relative intensities of the brushes do not vary greatly and their positions are fairly constant. When the sparking potential is reached the negative corona goes over into an arc very easily, much more easily, indeed, than is the case with the positive corona.

When the rectification of a corona is not complete, as is the case when various portions of the electromotive force wave are rectified, practically all combinations of a positive and negative corona discharge can be obtained. By using a small portion of the positive corona discharge it is possible to produce oscillatory sparks, these sparks being used to clean the electrodes of deposited material.

Inserting a spark gap and capacity in series with either a positive or a negative corona in the cylindrical precipitation chamber described above did not affect either kind of corona to any considerable extent, the observations being visual.

The accompanying Fig. III shows the negative corona, the camera being in the same position as that in which the positive corona was photographed. The electrical circuit was the same for both exposures, the direction of current only being changed. The outside cylinders were earthed. The actinic luminosity of the negative corona is very much less than that of the positive corona and is almost entirely confined to the region close to the active electrode. The number of bright points on the wire is seen to be much larger in the case of the negative corona. (The time of exposure of the negative and positive coronas was approximately the same.)

The results of the experiments are as follows:

(1) 1 cc. 1.042 NaOH solution neutralized in 12 minutes by a positive corona.

(2) 1 cc. 1.042 NaOH solution neutralized in 7.2 minutes by a negative corona.

(3) 1 cc. 1.042 NaOH solution neutralized in 13 minutes by a negative corona.

The energy consumption was about 300 watts and this would give about the same order of yield as is given by the Birkeland-Eyde, the Pauling and the Schönherr arc methods. Only a few runs were made as opportunity was afforded by the apparatus not being used for other purposes. It is hoped that a study of the ozone and nitric oxide yields under various conditions will furnish valuable information concerning the mechanism of these reactions, since we are able to partly control the ionic streams in these experiments.

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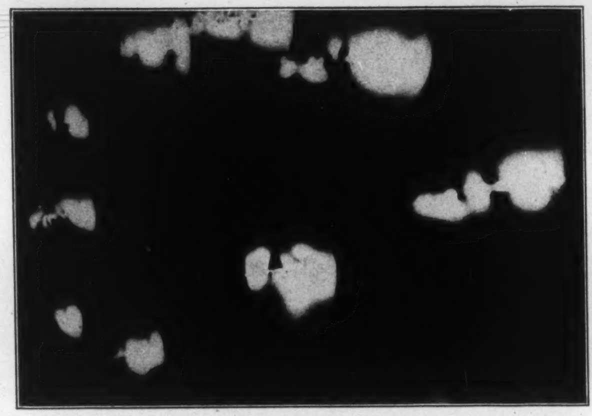

Fig. II

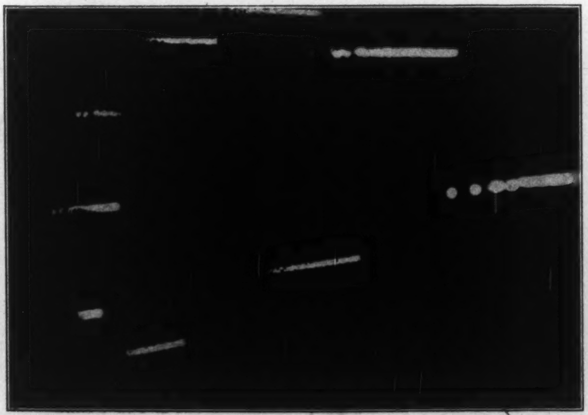

Fig. III

HIGH TENSION ELECTROLYSIS: A METHOD OF MEASURING HIGH VOLTAGE CURRENTS

By W. W. Strong

Among our most important laws connecting the phenomena of electricity and of matter are the laws of electrolysis. Indeed, it was through our knowledge of the conduction of electricity through electrolytes that the atomic nature of electricity was shown to be an actual fact. The relation between the amount of matter deposited at the electrodes and the quantity of charge which it has carried can be measured so accurately that the weight of this matter has been defined as being a measure of quantities of electricity.

Unfortunately one finds that very little quantitative work has been published concerning the phenomena of electrolysis when high voltages are used. One reason for this lack of data is due to the absence of sources of high and constant potential currents. It is well known that the potential given by an electrostatic machine is not constant (even though the circuit contain a comparatively large capacity) and the current available is almost infinitesimal in quantity. The so-called rectified currents possess electromotive force wave forms that are quite complicated and require much further study. Batteries such as small lead storage batteries are therefore practically the sole source of high tension potential currents and accurate experiments should be made to extend the ordinary laws of electrolysis to high voltage currents.

The arrangement of apparatus is indicated schematically in Fig. I.[1] A transformer, T, serves as a source of alternating voltage ranging between 5,000 and 60,000 volts. A graduated vessel, C', contains platinum electrodes E_1 and E_2 and a solution (about 0.1 normal sodium hydroxide in water was used) of electrolyte and is represented as being connected in series with the transformer and the corona wire A, the corona discharge being represented by C. When the potential reaches a certain value, a luminous glow appears on A and current flows between *A* and the grounded electrode *G E*. The cell *C′* may also be placed between *T* and the ground *G*. According to the above arrangement, the corona discharge from *A* is an alternating positive and negative corona. By using a rectifier such as *R* the corona current from *A* may be made positive or negative at all times.

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[1] For a fuller description see an article on Electrical Precipitation, J. Frank. Inst., Sept., 1912.

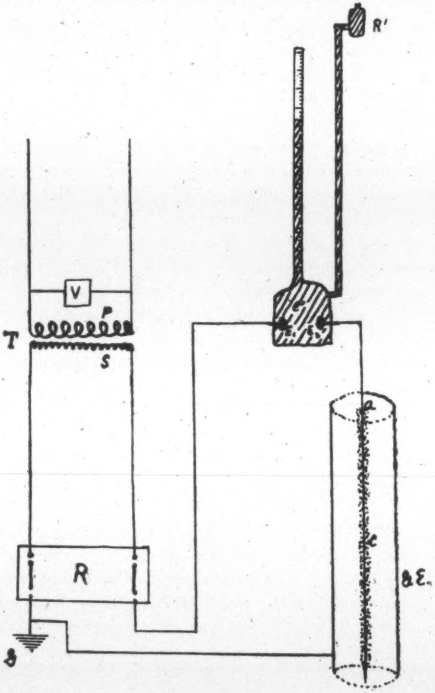

Fig. I

The direction of the current due to the corona will be represented by the direction of flow of the positive ions. When a unidirectional corona current is used the gas current is found to come almost entirely from the electrode in C′ that is positive. Hot gases can be passed through *C* and the amount of electrolysis measured for corona discharges in various kinds of gas. In the descriptive table the corona current due to a unidirectional corona depends upon the voltage and the portion of the wave form rectified.

(1) The gases are not given off at the electrodes according to the volume ratio ($2H_2 : O_2$). In many of the instances investigated practically all the gas moved in the same direction as the electric current.

(2) The total quantity of gas evolved was of the order of magnitude to be expected from Faraday's laws. In the present experiments[1] the form of the rectified current was not sufficiently well known to make possible the computation of the quantity of electricity carried.

(3) The currents used were the corona currents through a gas. The effective voltage varied between 10,000 and 35,000. When an alternating current was used, gas began to be liberated at a potential of about 17,000 volts effective. The flow of gas under these conditions was such as would make the positive corona current greater than the negative corona. This is in accord with the fact that for a given voltage the positive rectified corona current is greater than the negative rectified corona current.[2]

(4) The amount of electrolytic gas evolved appeared to depend upon the part of the circuit in which the cell was placed, Parts (16) and (17) of the table indicate this difference. On account of the sticking of the gas bubbles and the heating of the electrolytic solution (these solutions were boiled before being used) the experimental error was quite large. This error is probably not as great as that indicated in the following table.

(5) The electrolytic method promises to be of very considerable value in indicating the amount of rectification that exists in oscillatory and alternating currents and may be said

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[1] "The Positive and Negative Corona and Electrical Precipitation," P. Am. Inst. Elec. Eng., June, 1913.

[2] See paper on "The Positive and Negative Corona and Electrical Precipitation."

Corona Loss Experiments

	Gas evolved in cc. per min.	Sign of corona and voltage	Conditions of corona discharge	Remarks
(1)	0.029	Positive	Hot flue gas	Cell in series with rectifier and corona wire
(2)	0.031	Positive	Smoke	As above
(3)	0.037	Positive	Hot flue gas	As above
(4)	0.030	Positive	Hot flue gas	As above
(5)	0.0108	Alternating through rectifier gaps	Still room air	As above. Gas current is such as to make the active wire positive as above
(6)	0.0103	As above	Room air in motion	As above
(7)	0.026	Positive, 26,400 volts	Room air	As above. The gas current is nearly all in the direction of the current
(8)	0.0016	Positive, 36,000 volts	Negative electrode not grounded	As above
(9)	0.002	Alternating, no gaps, 38,000 volts	Still room air. One electrode free	As above. Gas current is such as to make the active wire positive

(10)	0.003	As above, 23,000 volts	Still air	As above. Gas current is such as to make the active wire positive
(11)	0.010	As above, 19,000 volts	Hot gases, 260°	As above. Almost all the gas current is such as to make the active wire positive
(12)	0.008	As above	Hot gases	Cell in series with the grounded wire. Gas current but slightly unidirectional
(13)	0.0232	Negative, 31,600 volts	Still room air	As above. Electrolysis was such as to indicate a negative corona
(14)	0.026	Negative, 31,600 volts	Hot air	As above
(15)	0.029	Positive, 22,500 volts	Hot air 260°	Cell in series with rectifier and corona wire
(16)	0.019	Positive	Still room air	As above
(17)	0.021	Positive	Still room air	Cell in series with the grounded electrode. Gas current in the direction of the electric current
(18)	0.027	Positive	Hot gases 260°	As above

to indicate changes in the medium in which the corona discharge is flowing. The corona current in (14) flows through hot gas, whereas in (13) it flows through room air. Apparently the corona current is the greater in the hot gas. When an alternating current is used, the corona is much more unidirectional in the hot gases, as is clearly shown in (9), (10) and (11).

(6) Placing the electrolytic cell on the grounded side of the corona discharge circuit seems to cause the electrolytic gas to be given off in the same way as for low voltage currents. This is indicated by (12).

EQUILIBRIUM IN THE SYSTEM: COBALT CHLORIDE AND PYRIDINE

BY J. N. PEARCE AND T. E. MOORE

Of the many possible systems containing as components pyridine, together with a single salt, only a comparatively small number have been studied in the light of the Phase Rule. The solubility method has been used for the investigation of systems containing the chloride,[1] bromide,[2] iodide[3] and nitrate[4] of silver, lead halides,[5] mercuric chloride[6] and lead nitrate.[7] Tombeck[8] used the vapor-pressure method in his study of compounds of copper salts with pyridine of crystallization. In an examination of some compounds of cobalt chloride with pyridine, Lang[9] believed that he obtained a product containing one molecule of Co_2Cl_4 to eight or ten molecules of pyridine. Reitzenstein[10] attempted to prepare compounds containing one, two and three to six molecules of pyridine to one molecule of cobalt chloride, but was unsuccessful. However, from cobalt chloride containing water of crystallization he made a compound which had the formula $CoCl_2.2C_5H_5N$. It had a bluish pur-

[1] Kahlenberg and Wittich: J. Phys. Chem., **13**, 421 (1909).
[2] Kahlenberg and McKelvey (not yet published).
[3] *Ibid.*
[4] Kahlenberg and Brewer: J. Phys. Chem., **12**, 283 (1908).
[5] Heise: *Ibid.*, **16**, 373 (1912).
[6] McBride: *Ibid.*, **14**, 189 (1910).
[7] Walton and Judd: J. Am. Chem. Soc., **33**, 1036 (1911).
[8] Tombeck: Ann. chim. phys., [7] **21**, 433 (1900).
[9] Lang: Ber. d. chem. Ges., **21**, 1578.
[10] Reitzenstein: Ann. Chem. (Liebig), **282**, 267.

ple color and melted at 192°–195°. By using anhydrous cobalt chloride he was able to obtain the cherry-red compound $CoCl_2.4C_5H_5N$. No other reference to compounds of cobalt chloride and pyridine could be found in the literature.

The possibility of a relatively large number of solid compounds of cobalt chloride with pyridine of crystallization made it seem worth while to make a systematic study of this system. For this purpose solubility determinations were made at frequent intervals throughout the maximum possible range of temperature.

Materials

Cobalt Chloride.—Kahlbaum's best grade of cobalt chloride was recrystallized from absolute alcohol. A saturated alcoholic solution was first made at about 75° and then quickly cooled to 0°; the product of fine crystals was quickly filtered upon a Buchner funnel, sucked as dry as possible and placed in a vacuum desiccator over phosphorus pentoxide. To insure complete desiccation the drying was continued in an electrically heated glass tube, first in a current of dry hydrogen chloride gas for eight hours and, finally, in a current of dry hydrogen gas for three hours, the temperature in both cases being 175°. The anhydrous cobalt chloride thus prepared was preserved in tightly stoppered weighing bottles in a desiccator over phosphorus pentoxide. In order to test its purity the cobalt was determined electrolytically; the results of the analyses of four separate samples gave the following percentages of $CoCl_2$:

100.00, 99.97, 100.04 and 100.07. Mean 100.02.

Pyridine.—Kahlbaum's chemically pure pyridine, which had been standing over fused caustic potash for at least six months, was distilled, every possible care being taken to exclude moisture. Only that fraction passing over in the temperature interval between 115°–116° under 742–743 mm. was used in this work.

Potassium Permanganate.—Kahlbaum's chemically pure salt was dissolved in sufficient distilled water to make an approximately 0.05 N solution. In order to make sure that all of the oxidizable organic matter was destroyed, the solution was allowed to stand for two weeks. It was then standardized by means of pure oxalic acid according to the usual method.

Oxalic Acid.—The oxalic acid solutions used for standardization of the potassium permanganate solution and for precipitating the cobalt oxalate were prepared from very pure oxalic acid which had been purified according to the method of Morse.[1]

Ethyl Alcohol.—The large stock supply of 50 per cent. alcohol used in the precipitation of the cobalt chloride and for washing was made by the dilution of the ordinary 95 per cent. alcohol.

EXPERIMENTAL

The solubility determinations were made in an apparatus somewhat similar to that first used by Meyerhoffer and Saunders.[2] The apparatus consisted of a large Jena glass test tube fitted with a rotating stirrer consisting of a glass rod to which was attached a spiral of heavy platinum wire. To prevent the entrance of moisture the stirrer was provided with a mercury seal. The whole was then inserted in a constant temperature bath.

For all determinations between 0° and 34°.6 a large water thermostat was used. By means of submerged electric lights, a cooling coil, a contact toluene regulator and telegraph relay, any desired temperature could be obtained and kept constant to within a few hundredths of a degree. Constant temperatures between 34°.6 and 110° were secured by inserting the saturation tube through a tightly fitting cork into a larger boiling vessel containing a pure liquid having a boiling point approximately equal to the temperature desired. The boiling vessel was also provided with two small tubules, one for the insertion of a standard Anschütz thermometer into the vapor and the other for a long upright condenser.

The liquid in the outer vessel was kept at the boiling temperature by means of an electrically heated coil of fine platinum wire, electrical contact being made by means of mercury and the current regulated by a bank of incandescent lamps. By using this apparatus it was possible to obtain temperatures constant to within 0°.10 for a period of twenty-four hours or more, the temperature being always that of the vapor of the boiling liquid and subject only to the change due to variation in barometric pressure. To further aid in keeping the temperature constant throughout the boiling chamber, the vessel was entirely covered with asbestos paper. Ice and salt in different proportions, moistened with distilled water, gave temperatures between 0° and —20°. By carefully varying the proportions of solid carbon dioxide and ether, constant temperatures were obtained between —20° and —50°.3. These low temperatures quickly change, but it was found that by continually adding small quantities of solid carbon dioxide even these low temperatures could be kept constant during the time required for saturation. The temperatures below —20° were read on a pentane thermometer which permitted estimations with an accuracy of 0°.10, while ordinary standard Anschütz thermometers, graduated to tenths of a degree and permitting estimations as exact as one one-hundredth of a degree, were used for all temperatures above 0°.

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[1] Morse: Exercises in Quantitative Analysis, p. 116.

[2] Z physik. Chem., 28, 464 (1899).

Saturation of the solution at any temperature was secured by rapidly stirring a mixture of the solid and liquid phases, the stirrer being driven by an electric motor and making about five hundred revolutions per minute. Samples of the liquid phase were removed at intervals of one hour and analyses made to insure saturation. Saturation was found to be complete in one hour, although the time allowed for saturation was, in most cases, about four hours. After saturation the stirrer was stopped and the crystals allowed to settle for about twenty minutes. The liquid was then drawn out in quantities of from two to five cc. by means of a long glass tube, the end of which was covered with a fine cloth filter to prevent the entrance of crystals. This was quickly introduced into glass-stoppered weighing bottles, allowed to reach the room temperature and then weighed. When the temperature of the saturated solution was higher than that of the room the sampling tube was heated slightly above the temperature of the solution to prevent solidification within the tube.

Method of Analysis

A number of methods were available for the determination of the cobalt, but none of these could be safely used in the presence of pyridine. At first the electrolytic determination of cobalt was attempted, using the ammonium formate method of Smith.[1] This is both rapid and accurate for aqueous solutions of cobalt chloride, but the presence of pyridine prevented the complete precipitation of cobalt. This method was consequently abandoned and others applied. However, in each case, the pyridine interfered with the results. Finally, it was found necessary, in every case, to evaporate off the pyridine before making an analysis. The following method was finally decided upon as the most accurate and reliable under the existing conditions.

The weighed sample of the solution contained in the weighing bottles was placed in an air bath and kept at a temperature of about 120° until no odor of pyridine remained. It was then transferred to a beaker and dissolved in 50 per cent. ethyl alcohol. Oxalic acid was added in excess, precipitating the cobalt oxalate. This was allowed to stand at room temperature for about thirty minutes to insure complete precipitation. Under these conditions the filtrate gave no indications of cobalt with ammonium sulphide. It was filtered and the precipitate washed with the 50 per cent. alcohol until the filtrate gave no test for oxalic acid with calcium hydroxide. The filter containing the precipitate was placed in an air bath and heated at a temperature of 100° until all the alcohol had been evaporated. The cobalt oxalate was then dissolved on the filter by means of sulphuric acid (diluted 1 to 3). After washing the filter thoroughly, the solution of cobalt sulphate and oxalic acid was diluted to about 300 cc., heated almost to boiling, and titrated directly with standard potassium permanganate. Since the cobalt solution is generally pink in color, it is obvious that only dilute solutions can be used for titration. With these there is no difficulty in determining the end point with permanganate. Samples containing greater concentrations of cobalt chloride were treated as before, diluted to a definite volume, and aliquot portions of these taken for analysis.

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[1] Smith: Electro-Analysis, p. 135.

To show the accuracy of the method, the data obtained in the determination of the purity of cobalt chloride are given in Table I. The weights of the cobalt chloride given in the second column are made up to 250 cc. and 50 cc. portions of this solution taken for each analysis. The mean percentage of cobalt chloride found agrees very closely with that obtained by the electrolytic method in the absence of pyridine.

Table I

No.	$CoCl_2$ present in gram	$KMnO_4$ cc. 0.04758 N	$CoCl_2$ found in gram	Error in gram	Per cent. $CoCl_2$ found
1	0.1389	45.05	0.1391	0.0002	100.14
2	0.1411	45.72	0.1410	0.0001	99.92
3	0.1453	47.09	0.1455	0.0002	100.13

Mean, 100.06

Mean of electrolytic determinations, 100.02

Solid Phases

The analysis of the solid phase was difficult in all cases. It was separated from the liquid by removing the stirrer from the tube and inserting a perforated platinum spoon by means of which crystals were lifted from the solution and allowed to drain within the tube at the exact temperature of equilibrium. The crystals thus obtained were freed from further adhering liquid by quickly pressing them between sheets of filter paper. They were then preserved in glass-stoppered bottles until analyzed. In order to ascertain their stability two samples of each solid phase were placed in desiccators, one over pyridine and the other in dry air. The difficulty in removing all the extraneous liquid from the crystals without the loss of pyridine from the compound itself gives results slightly high in pyridine, yet sufficiently accurate for determining the stoichiometric relations.

The freezing point of pure pyridine was found to be —48°.2 and that part of the curve between the latter temperature and —50°.3 is the freezing-point curve; *i. e.*, it represents the equilibrium between solid pyridine and the unsaturated solution. At —50°.3 the compound $CoCl_2.6C_5H_5N$ and solid pyridine separate out together, in contact with the liquid and vapor phases, and upon further cooling the entire mass solidifies. Since —50°.3 is the temperature at which the entire mixture freezes, there is no doubt that this temperature is very close to the true eutectic point. This point was found by placing the saturation tube in a Dewar flask containing solid carbon dioxide and ether and maintained at a temperature of about —65°. A thermometer and stirrer were inserted in the solubility tube and the mixture stirred slowly. The temperature gradually decreased until it was undercooled a few degrees, then it rose suddenly and remained at the temperature of —50°.3 until the mixture had entirely congealed, when the temperature again began to fall. This is a quadruple point, the invariant system consisting of four phases—solid pyridine, solid $CoCl_2.6C_5H_5N$, saturated solution and vapor.

The solubility remains practically the same with but slight increase from —50°.3 to +15°. The solid in equilibrium with the saturated solution between these temperatures has the composition $CoCl_2.6C_5H_5N$. These crystals are very minute and unstable, slowly giving up pyridine even in an atmosphere of pyridine. Owing to their rapid formation, the crystals were too fine to be identified even by means of a polarizing microscope. Their color is a bright pink bordering on the red.

The analysis of the crystals by two different methods, one for the pyridine content and the other for the cobalt chloride, agreed very closely. The crystals yielded 79.4 per cent. pyridine, while the calculated amount is 78.2 per cent. The high result is probably due to the pyridine adhering to the crystals.

From 15° to 70° the solubility gradually increases with rise in temperature. The solid phase now in equilibrium with the liquid has the composition $CoCl_2.4C_5H_5N$. These crystals are likewise very small, although somewhat larger than those of the previous compound. These also were too small to be accurately identified by the polarizing microscope. All that could be ascertained concerning their form is that they are not of the first system, and that they appeared to be hexagonal in shape. Their color is a very deep pink with a purplish cast. Upon analysis these crystals were found to contain 70.8 per cent. pyridine, whereas the theoretical value for the compound $CoCl_2.4C_5H_5N$ is 70.9 per cent. These crystals are quite stable in an atmosphere of pyridine, but when allowed to stand in dry air at ordinary temperatures gradually give up pyridine. At 15° we have another quadruple point at which there is equilibrium between the vapor, saturated solution, and the two solids $CoCl_2.6C_5H_5N$ and $CoCl_2.4C_5H_5N$.

Between 70° and 90° the solubility increases still more rapidly with the temperature. The solid now in equilibrium with the saturated solution has the composition $CoCl_2.2C_5H_5N$. It is composed of large monoclinic or triclinic crystals of the fifth or sixth order, having a purple color with a slightly bluish tint. Upon analysis they were found to contain 55.8 per cent. of pyridine, while the compound $CoCl_2.2C_5H_5N$ contains 55.0 per cent. At 70° we have a quadruple point, the four phases being vapor, saturated solution and the two solids $CoCl_2.4C_5H_5N$ and $CoCl_2.2C_5H_5N$.

From 90° to 110° the solubility increases very rapidly with relatively slight increase in temperature. The deep blue solid phase existing between these two points was found to be $CoCl_2$; it was found to be stable in pyridine-free air, but takes up pyridine rapidly when allowed to stand in an atmosphere of this solvent. The temperature 90° represents still another transition point at which vapor and the saturated solution are in equilibrium with the two solids $CoCl_2.2C_5H_5N$ and $CoCl_2$.

In order to test the relative stability of the four solid phases, *viz.*, $CoCl_2$, $CoCl_2.2C_5H_5N$, $CoCl_2.4C_5H_5N$ and $CoCl_2.6C_5H_5N$, samples of each were allowed to stand in a desiccator for three weeks over pyridine. Upon analysis all four gave results corresponding to the formula $CoCl_2.2C_5H_5N$, showing the latter to be the more stable at ordinary temperature.

The experimental results obtained are presented in Table II, which gives the number of grams of cobalt chloride per one hundred grams of solution and the number of grams of cobalt chloride soluble in one hundred grams of pyridine:

Table II

Composition of Liquid in Equilibrium with Solid $CoCl_2.6C_5H_5N$

Sample	Temp.	Time in hours	Weight sample	Weight $CoCl_2$ obtained	Gram $CoCl_2$ per 100 grams solution	Mean	Gram $CoCl_2$ per 100 grams pyridine	Mean
56	—50.3	1.2					0.42	
55	—45.0	1.2	2.2119	0.00926	0.4185	0.4185	0.4204	0.4204
52	—30.0	1.2	4.8486	0.02140	0.4194		0.4212	
53	—30.0	1.2	4.6014	0.01941	0.4217		0.4237	
54	—30.0	1.2	5.4849	0.02301	0.4204	0.4205	0.4222	0.4224
49	—19.6	1.4	4.8191	0.02031	0.4225		0.4243	
50	—19.6	1.4	6.1815	0.02466	0.3988		0.4007	
51	—19.6	1.4	7.0639	0.03114	0.4411	0.4208	0.4431	0.4227
46	—10.0	3.0	4.9500	0.02143	0.4330		0.4349	
47	—10.0	3.0	7.0530	0.03026	0.4290	0.4310	0.4309	0.4329
42	0.0	4.0	11.6558	0.05027	0.4307		0.4327	
43	0.0	4.0	4.8005	0.02062	0.4295		0.4314	
44	0.0	4.0	6.0773	0.02622	0.4313	0.4307	0.4338	0.4326

Transition Point

Composition of Liquid in Equilibrium with Solid $CoCl_2.4C_5H_5N$

Sample	Temp.	Time in hours	Weight sample	Weight $CoCl_2$ obtained	Gram $CoCl_2$ per 100 grams solution	Mean	Gram $CoCl_2$ per 100 grams pyridine	Mean
38	23.0	4.0	4.6116	0.02653	0.575		0.578	
39	23.0	4.0	6.7697	0.03865	0.571		0.574	
40	23.0	4.0	6.3204	0.05555	0.563		0.566	
41	23.0	4.0	5.2493	0.02981	0.568	0.569	0.571	0.572

57	25.0	3.5	4.8210	0.02777	0.576		0.579	
58	25.0	3.5	4.7322	0.02723	0.575		0.578	
59	25.0	3.5	5.8328	0.03345	0.574	0.575	0.577	0.578
1	34.6	4.0	3.6465	0.02749	0.754		0.760	
2	34.6	4.0	4.3187	0.03179	0.736		0.741	
3	34.6	4.0	5.0137	0.03750	0.748		0.754	
4	34.6	4.0	5.3414	0.04053	0.759	0.749	0.765	0.755
36	37.6	4.0	7.0387	0.05402	0.767		0.772	
37	37.6	4.0	5.3951	0.04030	0.742	0.754	0.748	0.760
5	44.6	5.0	5.1533	0.04777	0.927		0.936	
6	44.6	5.0	5.4246	0.05170	0.953		0.962	
7	44.6	5.0	5.3447	0.05072	0.949		0.958	
8	44.6	5.0	5.4241	0.05261	0.970	0.950	0.979	0.959
9	47.2	4.0	5.0138	0.05113	1.020		1.030	
10	47.2	4.0	5.0706	0.05288	1.043		1.050	
11	47.2	4.0	5.2199	0.05206	0.997		1.007	
12	47.2	4.0	4.8233	0.04918	1.008	1.020	1.028	1.029
32	51.0	6.0	4.3211	0.04791	1.109		1.121	
33	51.0	6.0	3.9030	0.04339	1.113	1.110	1.124	1.122
13	55.0	4.0	4.9569	0.05898	1.190		1.204	
14	55.0	4.0	5.127	0.06027	1.188		1.202	
15	55.0	4.0	4.7318	0.05670	1.198	1.192	1.213	1.206

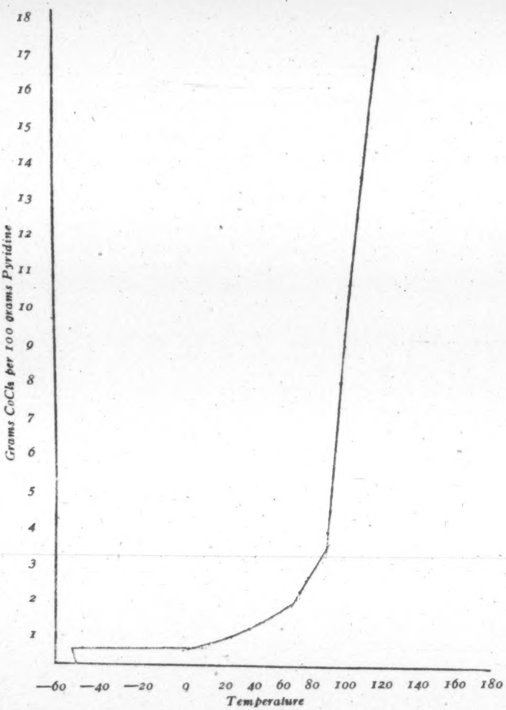
TABLE II—(*Continued*)

Sample	Temp.	Time in hours	Weight sample	Weight $CoCl_2$ obtained	Grams $CoCl_2$ per 100 grams solution	Mean	Grams $CoCl_2$ per 100 grams pyridine	Mean
16	60.0	4.0	5.3455	0.07080	1.324		1.342	
17	60.0	4.0	6.0555	0.08022	1.324	1.324	1.342	1.342
18	64.2	3.5	6.1928	0.09058	1.462		1.484	
19	64.2	3.5	2.9003	0.04232	1.459	1.460	1.482	1.483
60	68.0	3.0	4.7697	0.07555	1.584		1.609	
61	68.0	3.0	4.1115	0.06566	1.561	1.572	1.596	1.597
Transition Point								
Composition of the Liquid in Equilibrium with the Solid $CoCl_2.2C_5H_5N$								
34	74.8	3.0	2.7549	0.05634	2.045		2.087	
35	74.8	3.0	5.5110	0.11295	2.030	2.037	2.072	2.079
20	78.2	4.0	5.3976	0.12218	2.265		2.318	
21	78.2	4.0	5.9666	0.13645	2.288	2.276	2.342	2.330
62	79.8	4.0	3.2678	0.07955	2.431		2.492	
63	79.8	4.0	4.6397	0.11260	2.425	2.428	2.485	2.488
22	88.0	2.5	4.8881	0.16071	3.295		3.408	
23	88.0	2.5	3.2267	0.10550	3.272	3.284	3.387	3.397

Transition Point

Liquid in Equilibrium with Solid $CoCl_2$

24	96.5	5.0	3.8370	0.2775	7.234		7.796	
25	96.5	4.0	4.1234	0.2996	7.268	7.251	7.858	7.817
26	98.8	4.0	2.4947	0.1971	7.902		8.580	
27	98.8	4.0	2.4529	0.1955	7.970	7.936	8.661	8.862
28	106.0	3.0	1.0744	0.1321	(12.300)		(14.025)	
29	106.0	3.0	1.9391	0.2437	12.570		14.380	
30	106.0	3.0	1.4055	0.1765	12.570		14.380	
31	106.0	3.0	2.9736	0.3712	12.480	12.540	14.260	14.340
64	110.0	2.0	0.1012	0.01441	14.240		16.600	
65	110.0	2.0	0.2126	0.02993	14.090	14.165	16.398	16.500



Summary

The system cobalt chloride-pyridine has been studied for all temperatures between —50°.3 and 100°. The solubilities have been determined and the curve representing the equilibrium conditions established. It has been shown that cobalt chloride and pyridine form three distinct crystalline compounds. Reitzenstein had previously made the compounds $CoCl_2.2C_5H_5N$ and $CoCl_2.4C_5H_5N$, but the compound $CoCl_2.6C_5H_5N$ had not been isolated up to the present time. The compound $CoCl_2.2C_5H_5N$ was found to melt at from 195° to 200°, but we were unsuccessful in ascertaining the melting points of the other two, since they rapidly lose pyridine upon heating under atmospheric pressure.

The exact temperature limits within which these compounds can exist in equilibrium with a saturated solution have been determined. The compound $CoCl_2.6C_5H_5N$ exists as the solid phase between the temperatures —50°.3 and +15°, $CoCl_2.4C_5H_5N$ between 15° and 70°, $CoCl_2.2C_5H_5N$ between 70° and 90°, while between 90° and the boiling point of the saturated solution $CoCl_2$ is the stable, solid phase.

A new volumetric method for the determination of cobalt has been successfully applied.

PHYSICAL CHEMICAL LABORATORY
THE STATE UNIVERSITY OF IOWA
July, 1913

REPORTS

THE SPECTROSCOPE IN ORGANIC CHEMISTRY[1]

Somewhat more than half a century ago, while engaged, with the assistance of Faraday, in preparing experiments for a Friday evening discourse in this Institution, Stokes observed that the spectrum of the electric light extended to five or six times the length of the visible spectrum when he employed prisms and lenses of quartz instead of glass. This extension occurs at the violet end of the spectrum, and consists of rays of high refrangibility to which the eye is insensitive, but which can be made apparent by means of a fluorescent screen.

At the time of this discovery, and in the years immediately following it, attention was being directed to the absorption of light by colored solutions, and to the possibility of identifying colored substances by the number and position of the dark bands in the spectrum of light transmitted through their solutions. Stokes saw that by his discovery of the extension of the spectrum beyond the visible region, this method of investigation might be applied to colorless as well as to colored substances. In a paper communicated to the Royal Society in 1862, he says: "The mode of absorption of light by colorless solutions, as observed by the prism, affords, in many cases, most valuable characters of particular substances, which, strange to say, though so easily observed, have till very lately been almost wholly neglected by chemists." . . .

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[1] **Address delivered before the Royal Institution of Great Britain, April 4, 1913.**

"Having obtained the long spectrum above mentioned, I could not fail to be interested in the manner in which substances—especially pure, but otherwise imperfectly known organic substances—might behave as to their absorption of the rays of high refrangibility." He proceeded, therefore, to study the action of various organic solutions on the ultraviolet rays, and found that the mode of absorption generally was so constant and so characteristic that by this single property many substances could be identified. The substances which he examined included the best known vegetable alkaloids, all of which, with the exception of morphine and codeine, he was able to distinguish from one another by means of their absorption bands. This was a very remarkable anticipation of the results of later work on the subject, when we remember the great difficulties that must have been encountered in observing and measuring accurately the position of bands on a luminous screen.

While Stokes was engaged in these researches, Prof. William Allen Miller was simultaneously at work in the same field, and Stokes left the further development of the subject in his hands. Instead of a fluorescent screen, Miller employed a sensitive photographic plate for the reception of the spectrum. The rays of light were by this means made to register their own position and intensity, and a permanent record was obtained which could be studied at leisure. Miller failed, however, to "trace any special connection between the chemical complexity of a substance and its diactinic power." Struck by this fact, W. N. Hartley—now Sir Walter Hartley—commenced a systematic investigation of the whole subject, and it is to his researches, extending over a period of more than thirty years, that we owe, not only most of the knowledge which we now possess of the relation between the structure of organic substances and the action of such substances on the ultraviolet rays, but the elaboration of the convenient and elegant methods by which such investigations are now conducted.

The light derived from an ordinary source of illumination, such as an electric lamp, consists of waves of all degrees of refrangibility, and its spectrum shows a continuous band of color ranging from red to violet. The limits of this visible spectrum lie between the wave lengths 7600 and 3900.

If, instead of the electric light or other ordinary source of illumination, we employ the light emitted by one of the metals

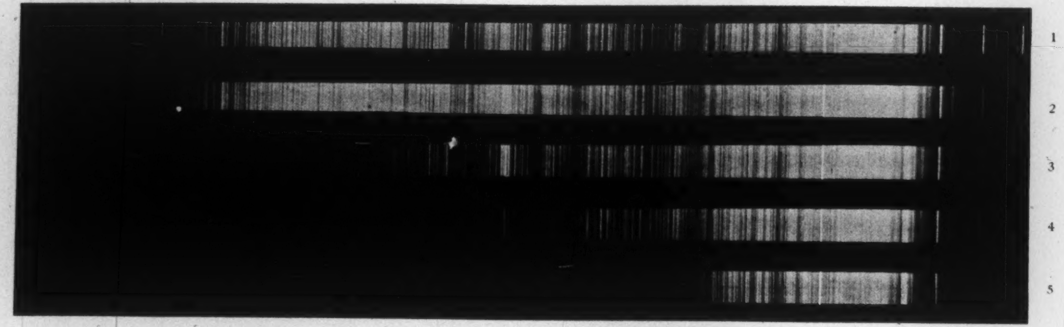

Fig. 1.—(1) Spark spectrum of nickel and iron; (2) the same after the light has passed through quartz, 10 mm. thick; (3) crown glass, 0.13 mm. thick; (4) crown glass, 0.33 mm. thick; (5) window glass, 1.62 mm. thick

when raised to a high temperature, the spectrum is seen to consist of a series of lines of different colors and intensities lying within the same limits as the visible spectrum. But there are rays beyond the red end of the spectrum and rays beyond the violet end which excite no sensation of luminosity in the eye. By allowing the spectrum to fall upon a screen which has been coated with a fluorescent substance, such as sulphate of quinine or a salt of uranium, these rays are rendered visible for a short distance beyond the violet. But it is only when we replace the glass apparatus, with which we have hitherto been working, by a quartz prism and lenses, and substitute a photographic plate for the eye, that the full extent of the spectrum beyond the violet is revealed (Fig. 1). This is the ultraviolet region—the region which Stokes opened up to investigation—and it is with the behavior of organic substances towards the rays of this part of the spectrum that we have mainly to do this evening.

When light is transmitted through a colored solution certain rays are absorbed, and dark bands corresponding to these rays appear in the spectrum. The importance of these bands as a means of distinguishing colored substances has long been recognized, and, as we have already seen, considerable progress had been made with their study fifty years ago. As the bands in this case are in the visible spectrum, no special means are required for their observation.

But when we extend this method of investigation to colorless substances, we are dealing with phenomena which lie hidden from the unaided eye, and our investigations are necessarily carried out with the help of photography.

The instrument employed in the study of absorption spectra consists of a spectroscope in which the eye-piece of the telescope is replaced by a camera. The photographic plate is set at such an angle as to bring all the rays emanating from the source of light into focus at its surface after they have passed through the resolving prism, and for this purpose it is necessary that the plate should have a very slight curvature. The prisms and lenses of the apparatus are made of quartz, which, unlike glass, is readily permeable by the ultraviolet rays. The source of light usually employed is that obtained by sparking one of the metals, such as iron, or a combination of metals, such as cadmium alloyed with lead and tin, selected so as to give a large number of lines spread as uniformly as possible over the whole ultraviolet region. The advantage of such a spectrum over a continuous spectrum is that the position of absorption bands, when they occur, can easily be determined with reference to the metallic lines whose wave lengths and place in the spectrum are known with great accuracy. In using the apparatus a photograph is first taken of the spectrum of the source of light. A layer of the substance to be examined, which, if a solid, must be dissolved in a suitable diactinic solvent, such as alcohol or water, is then interposed between the source of light and the slit of the collimator, and another photograph is taken. By comparison of the two photographs it is seen what effect, if any, the substance has had upon the transmission of the light.

When organic substances are examined in this way it is found that some allow light to pass freely through them. Others shorten the spectrum by absorbing the rays at the ultra-violet end to a greater or less extent, and are said to show general absorption. Others, again, possess the remarkable property of absorbing rays of a particular wave length, thereby producing gaps or bands in the spectrum; these are said to show selective absorption (Fig. 2).

In studying these phenomena in their relation to the chemical characters of a substance, it is of importance to determine not only the extent of the general absorption and the number and position of the absorption bands, but their degree of persistence, i. e., the range of concentration within which they are exhibited. It is necessary, therefore, to vary the concentration of the solution or the thickness of the layer so as to cover the whole phenomena of absorption. This is done by simply diluting the solution or diminishing the thickness of layer, on the one hand, until the entire spectrum is transmitted; and, on the other hand, by increasing the concentration or the thickness of the layer until no further characteristic absorptive effect is produced. Photographs (Fig. 3) are taken at each concentration, and a curve is drawn connecting the concentration and the absorption as measured with reference to the lines of the metal employed as a source of light. The values of the spectral lines are usually stated in wave lengths, but in these curves it is preferable to express them in reciprocals of wave lengths. It is also convenient to make use of the logarithms of the numbers representing the thicknesses of the layers examined, rather than the numbers themselves (Fig. 4).

If we now inquire whether the substances which affect light in one or other of the different ways already indicated have themselves anything in common, we find that it is with those which possess the structure characteristic of benzene and its derivatives that the power of absorbing the rays of particular parts of the spectrum is most frequently, although not exclusively, associated.

Organic compounds, or compounds containing the element

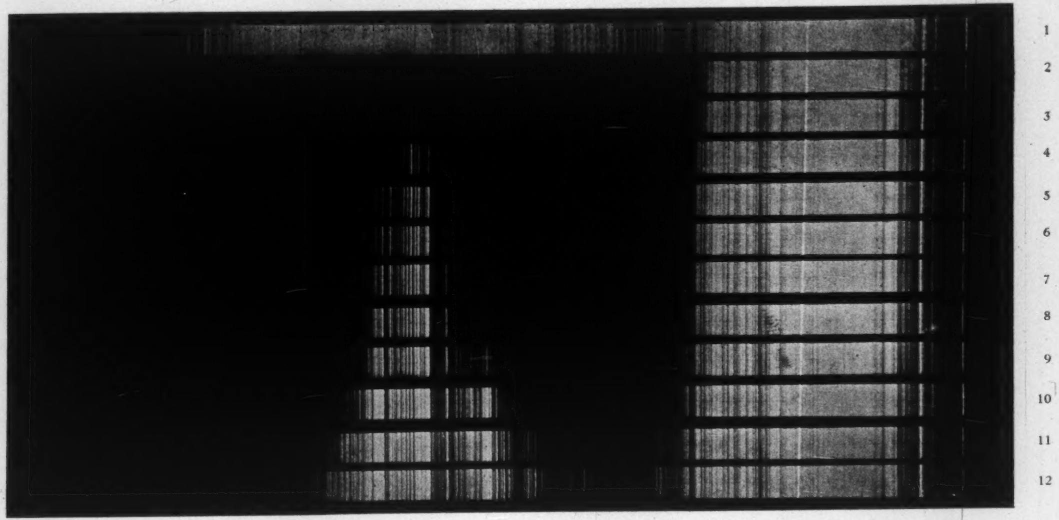

Fig. 3.—(1) Spark spectrum of nickel and iron; (2-12), the same after the light has passed through layers of 0.001 normal solution of salicylic acid from 90 to 4 mm. thick

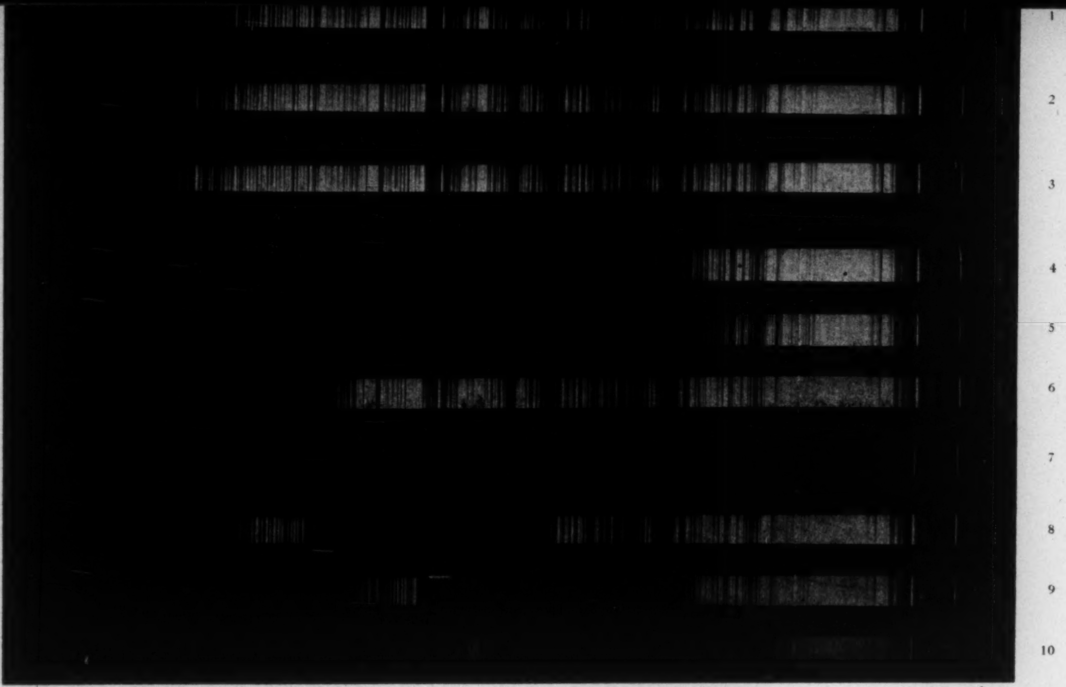

Fig. 2.—(1) Spark spectrum of nickel and iron; (2) and (3), the same after the light has passed through water and solution of cane sugar, respectively; alcoholic solutions of (4) pinene, (5) thiophene, (6) citric acid, (7) isatine, (8) phenol, (9) salicylic acid, (10) quinine hydrochloride; (4), (5) and (6) illustrate general absorption; (7), (8), (9) and (10) illustrate selective absorption

ol. 50
913

carbon, are divided into fatty or aliphatic, in which the carbon atoms are united in an open chain, and cyclic, in which the carbon atoms form a closed chain or ring. Hexane, which is a constituent of liquid paraffin, may be taken as an example of the first class. This substance possesses six carbon atoms united together in a single chain and having attached to them fourteen hydrogen atoms, giving as the formula of the compound C_6H_{14}. This substance is highly diactinic or transparent to the ultraviolet rays, and nearly all compounds belonging to the same division of organic chemistry, such as alcohols, sugars and fatty acids, are either equally transparent to light, or only cut off a portion of the extreme ultraviolet rays of the spectrum.

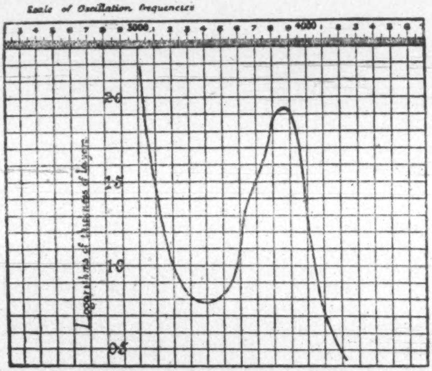

Fig. 4.—Salicylic Acid, 0.001 normal solution

If we now remove one atom of hydrogen from each of the two end carbon atoms of hexane, these atoms are in a condition to unite directly with each other, thus closing the chain. The substance so formed belongs to the cyclic division of organic compounds. It is known as cyclohexane, and has the formula C_6H_{12}, each carbon atom having two hydrogen atoms attached to it. This substance resembles hexane generally in its chemical properties, and behaves towards light in the same way; that is to say, it is practically diactinic or only cuts off some of the rays of light at the extreme ultraviolet end of the spectrum.

Speaking quite generally, it may be said that substances constituted like cyclohexane absorb more of the ultraviolet rather than those constituted like hexane.

But a wholly different condition is brought about if we suppose one atom of hydrogen removed from each of the six carbon atoms of cyclohexane. One linkage is thus set free in each of the six carbon atoms; and we obtain benzene. How these linkages are actually employed in benzene has never been determined with certainty. Sometimes they are represented as mutually neutralizing one another, sometimes as effecting a double link between the alternate pairs of carbon atoms. However this may be, the structure which bears the relation that I have indicated to the structure of hexane and cyclohexane is characteristic of the large group of organic substances of which benzene is the type. It is to this division of the cyclic compounds that the great majority of substances which show selective absorption, i. e., produce breaks or dark bands in the spectrum, belong. Here, then, we have a very important and a very general relation between the structure of organic substances and their absorption spectra.

The difference in the behavior of organic substances towards the ultraviolet rays, as exemplified in hexane and cyclohexane, on the one hand, and benzene on the other, is brought out very clearly when we examine some of their derivatives. If we replace an atom of hydrogen in hexane or cyclohexane by the monovalent group hydroxyl, we get substances belonging to the class of alcohols, and these substances are, like their parent substances, highly diactinic. If, on the other hand, we replace an atom of hydrogen in benzene by the same group we get carbolic acid or phenol, which, like benzene, exercises selective absorption on the ultraviolet rays, but gives a spectrum widely different from that of benzene.

Having dealt with the most general relation that has been observed between the structure of organic substances and their action on the ultraviolet rays, I propose to illustrate some of the more special relations by examples from the phenomena of isomerism. By replacing an atom of hydrogen in carbolic acid or phenol by the nitro group we obtain three distinct nitrophenols. The ultimate particles or molecules of these nitrophenols are all composed of the same elements, carbon, hydrogen, oxygen and nitrogen, and of the same number of atoms of each element. Such substances are said to be isomeric, i. e., they are made up of equal parts, although they do not possess the same properties. The difference between them lies in the arrangement of the parts relatively to each other; in this case in the position of the nitro group in relation to the hydroxyl group. On comparing the spectra of the three nitrophenols we find that they differ in quite a marked manner from one another, and afford an illustration of the important general rule that substances which have the same composition give different spectra if they differ in structure, i. e., in the arrangement of the atoms of their molecules.

It will have been noticed that the substitution of the nitro group for hydrogen in phenol has the effect of shifting the absorption band nearer to the visible region. One of the three nitrophenols has a yellow color, and in this case the gap in the spectrum cuts a little way into the violet end of the visible region. By the addition of soda to the solution the color is changed to red, and on examining the spectrum of this solution we see that the gap now extends far into the visible region. This example will serve to illustrate the close connection that exists between the study of absorption spectra and the origin of color, an interesting branch of the subject with which, however, it is impossible for me to deal within the limits of this discourse.

In the nitrophenols we have an example of what is known as structural isomerism, or position isomerism, because the phenomenon depends upon differences in the position or arrangement of the atoms within the molecule—in other words, on the internal structure of the molecule. But it is possible to have two substances of the same composition and structure not identical, but related to one another as an object is to its mirror image. Substances so related are termed optical isomers or stereoisomers. The spectra of isomers of this class, unlike those of structural isomers, do not differ. This leads to an important application of absorption spectra in chemical investigations. If two substances have the same composition but different spectra, we know that they must be structurally different; if, on the other hand, they have the same composition and the same spectra, and yet are not identical, there is a strong probability, although not a certainty, that they are optical isomers. To take an example: we know three substances of vegetable origin—papaverine (from opium), canadine (from the roots of *Hydrastis canadensis*), and tetrahydroberberine (a derivative of the principal alkaloid obtained from species of the barberry)—which have the same chemical composition represented by the formula $C_{20}H_{21}O_4N$. Papaverine and canadine differ widely in their spectra and in their structure; canadine and tetrahydroberberine have identical spectra, from which we should infer that they are in all probability stereoisomers, a conclusion which has been independently established by the most satisfactory chemical evidence.

In applying this reasoning in the investigation of substances of unknown structure, it has always to be borne in mind that while we may safely infer from dissimilarity of spectra dissimilarity of structure, we cannot always infer similarity of structure from similarity of spectra.

The study of absorption spectra has proved of special value in the investigation of substances capable of existing in two forms which may pass from the one into the other. It is rarely the case that both forms of such substances are stable, and it is often extremely difficult, or altogether impossible, on account of this instability to determine, by the ordinary chemical processes, which of the two possible forms the substance as we know it possesses. Such substances, however, frequently give rise to two series of stable isomeric methyl or ethyl derivatives, whose structure can be ascertained by chemical investigation. The parent substance, if not a mixture of the two forms, must correspond in structure with one or other of these derivatives, because it is a well-established fact that the introduction of the methyl or ethyl group into a substance in place of an atom of hydrogen does not appreciably alter the spectrum.

An example of this is afforded by the three substances isatine, methylisatine, and methylpseudoisatine. The structure of methylisatine and of methylpseudoisatine has been determined by chemical methods, but the structure of the parent substance isatine cannot be determined in this way. Is it constituted like methylisatine or like methylpseudoisatine? Inspection of the photographs of the spectra of the three substances shows that while there is a wide difference between the spectra of isatine and methylisatine, the spectra of isatine and methylpseudoisatine are almost identical, as we should expect them to be on the view that they are constructed alike.

This phenomenon, which is known as tautomerism, is due to the fact that some substances contain an atom of hydrogen or it may be a hydroxyl group, which readily shifts in position within the molecule, leaving its union with one atom to attach itself to another. Another example of this is afforded by cotarnine, a substance found in opium. The molecule of cotarnine possesses an atom of carbon which is directly combined with an atom of nitrogen, and has also united to it a hydroxyl group. Under the influence of certain reagents the hydroxyl group leaves the carbon atom and attaches itself to the nitrogen atom, but can readily, by an alteration of the conditions, be enticed back again to the carbon atom. The shifting of the position of the hydroxyl group is accompanied by other changes which, however, it is not necessary that we

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should take into account for our present purpose. In this case both of the tautomeric forms are, under certain conditions, stable. The form in which the hydroxyl is attached to the carbon is colorless, while the form in which it is attached to the nitrogen is yellow. The two forms have totally distinct absorption spectra. When one of the forms passes into the other under the influence of the appropriate reagent, the amount of change is proportional to the quantity of reagent added. It is possible, therefore, by taking photographs after the addition of each successive quantity of reagent to trace the progress of the change through all its phases, and to ascertain how much of each form is present at any time. This is done by comparison with a series of reference plates prepared by photographing mixtures in various definite proportions of two derivatives of cotarnine which possess the same spectra as the two parent forms.

Incidentally I may mention that these changes afford a basis for the measurement of the relative strength of alkalis and acids. For example, the change from the yellow to the colorless form of cotarnine takes place under the influence of alkalis, and by comparing the amount of change produced by equivalent quantities of different alkalis we obtain a measure of their strength.

The spectrographic method of investigation has been applied with marked success to the study of the vegetable alkaloids. Many of these substances, such as quinine, morphine, strychnine and atropine, possess powerful and valuable physiological properties, and their careful investigation is of the greatest importance to medical science. The number of atoms present in the molecule of an alkaloid is nearly always large, frequently as many as fifty or sixty. It is obvious, therefore, that the task of determining their exact relation to one another must be one of no little difficulty, and as a matter of fact the elucidation of the structure of an alkaloid is one of the hardest problems that the organic chemist can set himself. Any method, therefore, which assists the chemical examination is of peculiar value in this branch of organic chemistry.

In investigating an alkaloid or any organic compound, the first thing that the chemist has to do is to determine the elements of which it is composed, and the number of atoms of each of those elements present in one of its molecules or ultimate particles; in a word, what is known as its molecular formula. This is a comparatively easy operation: the difficulty comes when he attempts to determine the structure of the molecule, i. e., the exact manner in which the atoms are arranged with respect to one another. Now it may happen that two or more alkaloids have the same, or nearly the same, composition. The question arises, are they constructed on the same plan? It is in attempting to answer this question that the value of the spectroscope asserts itself. If on dissolving the alkaloids in some diactinic solvent and photographing their absorption spectra we find that the spectra are wholly different, we may conclude that in spite of the similarity, or even identity in their composition, the substances are not intimately connected with one another. If, on the other hand, we find that the spectra are the same, or very similar, it is probable that the substances are closely related. If the composition is the same and the spectra are the same, the substances are almost certainly optical isomers. Of substances related in this way we have already had an example in papaverine, canadine and tetrahydroberberine.

Among the rare alkaloids of opium are two, to which the names of laudanin and laudanosin, respectively, have been given. They have nearly, but not quite, the same composition, laudanosin containing one atom of carbon and two atoms of hydrogen more than laudanin; in other words, it is a homologue of laudanin. Substances so related hardly differ in their spectra, the replacement of one atom of hydrogen by the group of atoms CH_3 having very little disturbing influence, as we have already seen, upon the structure of a substance or upon its power of absorbing light. The spectra of laudanin and laudanosin being practically the same, it was inferred that they possessed the same structure and were probably homologous, before the fact had been ascertained by the usual chemical examination.

I must here advert again for a moment to Stokes' work on absorption spectra. I mentioned at the outset that he had been able to distinguish all the alkaloids he examined from one another by means of their absorption bands, except morphine and codeine. At that time the relation of these alkaloids to one another was unknown. We now know that they are homologues, and in that fact have the explanation of Stokes' failure to distinguish them by their absorption bands, and at the same time a striking testimony to the accuracy of his observations.

The examination of the spectra of laudanin and laudanosin not only revealed the fact that the two substances are homologues, but gave a clear indication as to the group of alkaloids to which they are most closely allied. When the spectra were compared with those of other alkaloids, they were found to resemble the spectra of corydaline and the related alkaloids so closely as to leave very little room for doubt that they are built on the same plan as these alkaloids. At the same time that

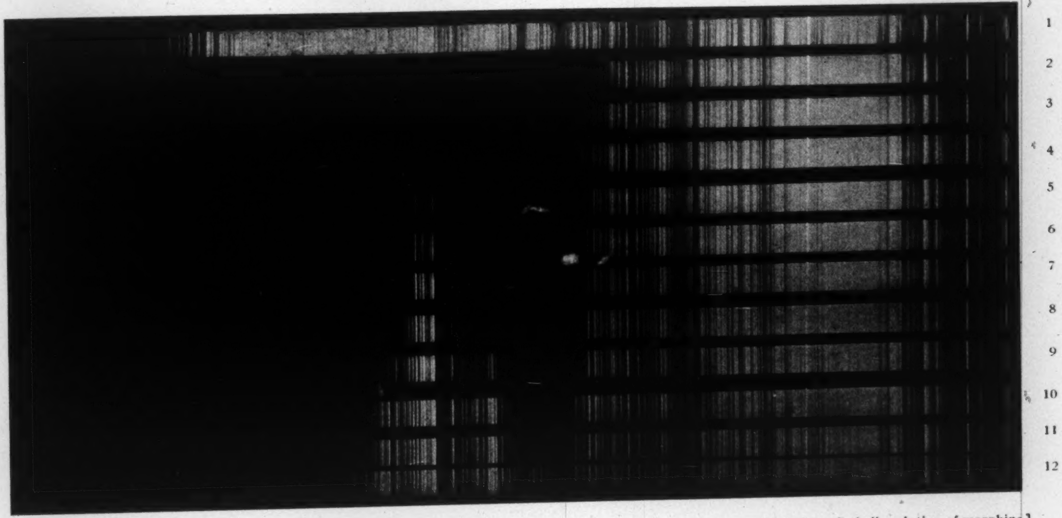

Fig. 5.—(1) Spectrum of nickel and iron; (2-12), the same after the light has passed through layers from 60 to 4 mm. thick of an alcoholic solution of morphine containing 1/200 grain of the alkaloid

this conclusion was arrived at, practically nothing was known as to the chemical structure of laudanin and laudanosin, but the inference as to their close association with corydaline was subsequently fully justified by chemical investigation.

Apart from their structure there is another point of view from which the study of the spectra of the alkaloids is of interest and importance. These substances generally have very characteristic spectra by means of which they can be distinguished with certainty from one another, except when they are homologous or otherwise very closely related. The spectroscopic method may, therefore, be used with great advantage in examinations for the presence of alkaloids to confirm the results obtained by the usual chemical tests. The chemical tests are no doubt as a rule sufficiently distinctive, but considering the gravity under which they have frequently to be applied, it is unnecessary to insist on the value of the confirmatory evidence which can be obtained by the use of the spectroscope.

The minutest quantities of alkaloids can be detected by this means, the method rivalling the color reactions for the alkaloids in delicacy. Thus, with a quantity of strychnine not exceeding 0.002 of a grain, a clearly defined spectrum of the alkaloid can be obtained. The photograph of morphine already shown was obtained with 0.005 of a grain of the alkaloid (Fig. 5), and that of nicotine with 0.01.

The spectroscope serves not only for the detection, but for the estimation of alkaloids; by comparing the spectrum obtained with an unknown quantity of an alkaloid with a series of spectra obtained by photographing known quantities of the same alkaloid, it is possible to make quantitative determinations of a high degree of accuracy.

The use of the spectroscope in the detection and estimation of alkaloids in cases of poisoning possesses certain advantages of the highest importance. One is that the material is not destroyed. The solution which has been employed for the spectroscopic examination can be used afterwards for the chemical examination. Another is that a permanent record is obtained which is always available for reference.

So far my illustrations have been confined almost entirely to colorless substances, because it is in connection with the investigation of such substances that most of the recent advances in the subject have been made.

As my last example, I shall take the case of a colored substance in which the method has been applied within the last year with marked success.

It will be remembered that considerable uneasiness was caused when it became known sometime ago that nitrogen peroxide is sometimes employed to bleach flour. In the course of an inquiry into the subject, it became necessary to determine the nature of the coloring matter naturally present in flour. It was known that many of the yellow and orange pigments, so widely distributed throughout the vegetable kingdom, are either closely connected or identical with carrotene, the orange coloring matter of carrots, and it had been suggested that the coloring matter of unbleached flour might be identical with, or belong to the same class of coloring matters as this substance. It was impossible, however, to prove this by the usual chemical methods, because the amount of coloring matter in flour is so minute that its isolation in a pure state, and in sufficient quantity for chemical analysis, was hardly practicable. Carrotene, however, can be prepared in a pure state, and the happy idea occurred to Dr. Monier Williams, of the Local Government Board, who was conducting the investigation, to photograph its absorption spectrum and compare it with that of the coloring matter of flour, which could easily be obtained in the minute quantity required for this purpose. Inspection of the photographs shows that the spectra are very similar. There cannot, therefore, be any doubt that the coloring matter of flour, if not identical with, is closely allied to carrotene.

The underlying causes of the relations between chemical structure and absorption spectra have been the subject of much speculation. Hartley considers that the phenomena of absorption are intimately connected with the vibration of the atoms within the molecule. This view has much to recommend it, but obviously its application is limited by the present imperfect state of our knowledge of the internal mechanism of the molecule. A theory has been advanced according to which absorption bands are only exhibited by compounds whose molecules are in a state of change or flux. In the case of benzene, for example, the old idea is revived that the carbon atoms are linked together by alternate double and single bonds, which are perpetually changing positions. The presence of the bands in the spectrum of benzene is supposed to be in some way connected with these changes. Substances, however, are known which have banded spectra in regard to which such an explanation is inadmissible.

Quite recently a promising attempt has been made to bring the production of banded spectra into relation with the theory of electrons.

It must be confessed, however, that no satisfactory explanation of the phenomena of absorption has yet been formulated, and that the theoretical development of the subject lags behind its practical application. JAMES J. DOBBIE

SOME FURTHER APPLICATIONS OF THE METHOD OF POSITIVE RAYS[1]

The method to which I shall refer this evening is the one I described in a lecture I gave here two years ago. The nature of the method may be understood from the diagram given in Fig. 1. A is a vessel containing the gases at a very low pressure; an electric discharge is sent through these gases, passing from the anode to the cathode C. The positive electrified particles move with great velocity towards the cathode; some of them pass through a small hole in the center, and emerge on the other side as a fine pencil of positively electrified particles. This pencil is acted on by electric forces when it passes between the plates L and M, which are connected with the terminals of a battery of storage cells, and by a magnetic force when it passes between P and Q, which are the poles of an electromagnet. In the pencil before it passed under the influence of these forces there might be many kinds of atoms or molecules, some heavy, others light, some moving quickly, others comparatively slowly, but these would all be mixed up together. When they are acted on by the electric and magnetic forces, however, they get sorted out, and instead of traveling along the same path they branch off into different directions. No two particles will travel along the same path unless

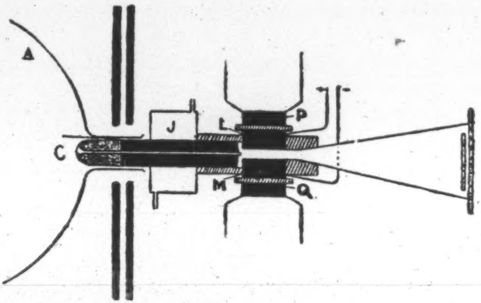

Fig. 1

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[1] Address delivered before the Royal Institution of Great Britain, January 17, 1913.

they have the same mass as well as the same velocity; so that if we know the path of the particle we can determine both its mass and its velocity. In chemical analyses we are concerned more with the mass than with the velocity, and we naturally ask what is the connection between the paths of particles which have the same mass but which move with different velocities. The answer is that all such paths lie on the surface of a cone, and that each kind of particle has its own cone; there is one cone for hydrogen, another for oxygen, and so on. Thus one cone is sacred to hydrogen, and if it exists there must be hydrogen in the vessel; so that if we can detect the different cones produced from the original pencil, we know at once the gases that are in the tube. Now, there are several ways of identifying these cones, but I shall only refer to the one I have used in the experiments I wish to bring before you this evening. These moving electrified particles, when they strike against a photographic plate, make an impression on the plate, and a record of the place where they struck the plate can be obtained. Thus, when a plate is placed in the way of the particles streaming along these cones, the sections of these cones by the plate (parabolas) are recorded on the photograph, hence we can identify these cones by the parabolic curves recorded on the photograph, and these parabolas will tell us what gases are in the vessel.

The first application of the method which I shall bring before you this evening is to detect the rare gases in the atmosphere. Sir James Dewar kindly supplied me with two samples of gases obtained from the residues of liquid air; the samples had been treated so that one might be expected to contain the heavier gases, the other the lighter ones. I will take the heavier gases first. The photograph for these is shown in Fig. 2. When the plate is measured up it shows a faint line corresponding to the atomic weight 128 (xenon), a very strong line corresponding to the atomic weight 82 (krypton), a strong argon line 40 (argon), and the neon line 20. There are no lines unaccounted for, and hence we may conclude that in the atmosphere there are no unknown gases of large atomic weight occurring in quantities comparable with those of xenon or krypton. This result gives an example of the convenience of the method, for a single photograph of the positive rays reveals at a glance the gases in the tube. I now turn to the photograph of the lighter constituents shown in Fig. 3; here we find the lines of helium, of neon (very strong), of argon, and in addition there is a line corresponding to an atomic weight 22, which cannot be identified with the line due to any known gas. I thought at first that this line, since its atomic weight is one-

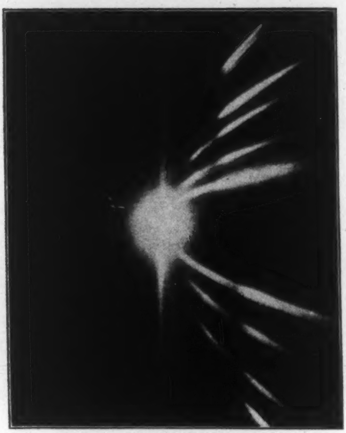

Fig. 2

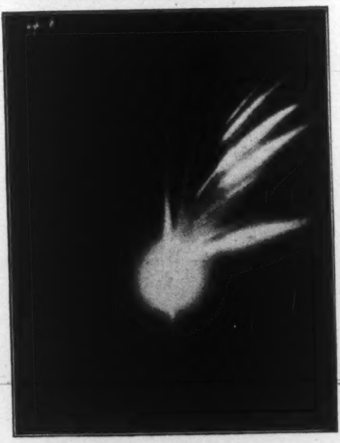

Fig. 3

half that of CO_2, must be due to a carbonic acid molecule with a double charge of electricity, and on some of the plates a faint line at 44 could be detected. On passing the gas slowly through tubes immersed in liquid air the line at 44 completely disappeared, while the brightness of the one at 22 was not affected.

The origin of this line presents many points of interest; there are no known gaseous compounds of any of the recognized elements which have this molecular weight. Again, if we accept Mendeléeff's Periodic Law, there is no room for a new element with this atomic weight. The fact that this line is bright in the sample when the neon line is extraordinarily bright, and invisible in the other when the neon is comparatively feeble, suggests that it may possibly be a compound of neon and hydrogen, NeH_2, though no direct evidence of the combination of these inert gases has hitherto been found. I have two photographs of the discharge through helium in which there is a strong line, 6, which could be explained by the compound HeH_2, but, as I have never again been able to get these lines, I do not wish to lay much stress on this point. There is, however, the possibility that we may be interpreting Mendeléeff's law too rigidly, and that in the neighborhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel and cobalt. From the relative intensities of the 22 line and the neon line we may conclude that the quantity of the gas giving the 22 line is only a small fraction of the quantity of neon.

Let me direct your attention again to the photograph of the heavier gases in the atmosphere. You will notice that the parabolas corresponding to many of the elements start from points which are all in the same vertical line; this indicates that the atoms or molecules which form these parabolas all carry the same charge. Several of these lines, however, do not follow this rule; you will notice, for example, that the neon line has a prolongation which comes nearer than the normal line to the vertical line drawn through the undeflected spot. Measurement of the photograph shows that the neon line begins at a distance from this vertical line which is only half the normal distance; this shows that some of the neon atoms in the positive rings possess two charges of electricity; the majority of them, however, possess only one. If you examine the argon line you will find that it comes even nearer to the vertical than the neon line; in fact, it begins at a distance from the vertical only one-third of the normal distance; this proves that the argon atom can have as many as three charges of electricity. If now you examine the krypton line you will find that it comes nearer to the vertical line than even the argon; its least distance is one-fourth of the normal distance, showing that the krypton atom may have as many as four charges. The mercury line comes so close to the vertical line that it is only on large photographs that it can be seen that there is in reality an interval; this interval is only one-eighth of the normal interval, showing that mercury may acquire eight positive charges, i. e., that it may lose eight corpuscles. The mercury atom when it is on this line must have only the normal charge, i. e., it must have regained all but one of the corpuscles it previously lost; if it had retained two positive charges it would have been on the line corresponding to the atomic weight 200/2 or 100; if it had retained 3, or 4, 5, 6, 7, 8, on the lines corresponding to the atomic weights, 200/3, 200/4, 200/5, 200/6, 200/7, 200/8, respectively. All these except the last have been detected on the plate. The lines corresponding to the multiple charges on krypton, argon and neon have also been detected. It appears, then, that in a vacuum tube a mercury atom, for example, may be ionized in two ways; in the one way the atom loses one corpuscle, in the other it loses eight. I would suggest that these two types of ionization may result from the two different types of collision which the atom must experience. The first type is collision with a corpuscle; since the corpuscle is an exceedingly small body moving with a very great velocity, it can pass freely through the atom, and the collision it makes with the atom is really a collision with a corpuscle inside the atom; this may result in the corpuscle it strikes acquiring such a great velocity that it is able to escape from the atom; this type of collision will result in the detachment of a single corpuscle. The second type of collision is when the atom collides with another atom and not with another corpuscle; the result of this collision may be that the atom suffers a sudden change in its velocity. This change is not at first shared by the corpuscles, so that these just after the collision may have a very considerable velocity relative to the atom. If there are several corpuscles which are comparatively loosely attached to the atom, these may all be detached from it and leave it with a positive charge corresponding to the number shaken out. It is this type of collision which we regard as giving the multiply-charged ions, and we see that the magnitude of the charge is a measure of the number of corpuscles in an atom which are readily detachable from it. We have seen that the greater the atomic weight the greater the charge it can acquire, the maximum charge being roughly proportioned to the square root of the atomic weight, hence the heavy elements have a larger number of detachable corpuscles than the lighter ones.

Another application of the method I should like to bring before you is the use of it for the discovery and investigation of a new substance. I have in previous lectures said that sometimes there appeared on the plates a line corresponding to a particle with an atomic weight 3; this must either be a new element or a polymeric modification of hydrogen, represented by H_3. The other possibility that it is a carbon atom with four charges is put out of court by the fact that it frequently occurs when the carbon line is exceedingly faint, and when there is not a trace of a carbon atom with even two charges, though the doubly-charged carbon atom occurs readily under certain conditions. In addition to this, the carbon atom parabola never approaches the vertical near enough to allow of its having four charges. I thought the study of the substance producing this line would be of interest, and I have for some time been working at it, and although the research is by no means completed, I have obtained some results which I should like to bring before you.

At first I was greatly hindered by not knowing the conditions under which the line occurred; although it appeared from time to time on the plates, its appearance was always fortuitous and sometimes for weeks together the plates would not show a trace of the line. The line sometimes appeared, but why it did so was a mystery, and I could not get it when I wanted it. I began an investigation, which proved long and tedious, to find the conditions under which the line appeared. I tried filling the discharge vessel with all the gases and vapors described in the books on chemistry without success. At last I tried bombarding various substances with cathode rays. Under this treatment the substances give off considerable quantities of gas, the greater part of which is hydrogen, carbonic acid or carbon monoxide. When I came to analyze by the positive rays the gases given off in this way, I found that with a large number of substances these gases contained the substances giving the three lines, so that I was now in a position to get this line whenever I wanted it, and investigate the properties of the gas to which it owes its origin. The question of the gases absorbed and given off by solids is an extremely interesting one, and a considerable number of investigations have been made on it. In all these, as far as I know, the method has been to heat the solid to a high temperature, and then measure and analyze the very considerable amount of gas which is driven off by the heating. As far as I know, no experiments have been made in which the gases were driven off by bombardment with cathode rays. This treatment, however, will cause the emission of gas even when ordinary heating fails to do so.

Belloc, who has recently published[1] some interesting experiments on this subject, after spending about six months in a fruitless attempt to get a piece of iron in a state in which it would no longer give off gas when heated, came to the conclusion that, for practical purposes, a piece of iron must be regarded as an inexhaustible reservoir of gas. There are some interesting features about the emission of gas from a heated solid. If the body is kept for a long time in a vacuum at a high temperature, the emission of gas becomes too small to be detected; if after this treatment the temperature is raised considerably, there will be a further copious emission of gas, which again diminishes as the heating continues. After it has fallen to zero, all that is necessary is to raise the temperature again and you will get a fresh supply of gas; and as far as my experience goes, after you have got all the gas you can out of the solid by heating it, you have only to expose it to cathode rays to get a fresh outburst. This effect of increased temperature in renewing the stream of gas from the solid seems to me to be too large to be accounted for merely by an increase in the rate of diffusion of the absorbed gas from the interior to the surface; it seems to be more analogous to the case of the emission of the water of crystallization from some salts. There are some salts, for example, copper sulphate, which when heated lose their water of crystallization in stages; thus, if the temperature is raised to a certain value, some of the water of crystallization comes off, but the rest remains fixed, and you may keep the salt at this temperature forever without getting rid of all the water of crystallization; on raising the temperature, however, fresh water of crystallization is given off. Something of this kind seems to take place in the case of gases absorbed in metals, and there seem to be indications that there is some kind of chemical combination between the gas and the metal. This absorbed gas may influence the behavior of the substance. For example, an ordinary carbon filament gives off, when raised to a white heat, large quantities of negatively electrified corpuscles; but Pring and Parker[2] have shown that when great precautions are taken to get rid of the absorbed gas, the emission of these corpuscles falls to less than one-millionth of their previous value. It is in the gases given off by certain metals when they are bombarded by cathode rays that I have found an unfailing source of the substance, which I shall denote by X_3, giving the line corresponding to the atomic weight 3. The arrangement I have used for investigating the presence of this gas is shown in Fig. 4. A is a vessel communicating with the bulb B, in which the positive rays are produced, by two tubes, one of which is a very fine capillary tube, while the other one is five or six mm. in diameter; taps are inserted so that one or both of these vessels can be closed, and the vessels A and B isolated from each other. A is provided with a curved cathode such as are used for Röntgen ray focus tubes, and the cathode rays focus on the platform on which the substance to be bombarded is placed. [It is not absolutely necessary to focus the cathode rays in this way, but it makes the supply of the gas X_3 more copious.] After the metal or other solid to be examined has been placed on the platform, the taps between A and B being turned so as to cut off the connection between them, A is exhausted until the vacuum is low enough to give the cathode rays; the discharge is then sent through A, and the cathode rays bombard the solid. The result of this is that in a few seconds so much gas, mainly carbon dioxide and hydrogen, is driven out of it that the pressure gets too high for the cathode rays to be formed, and unless some precautions to lower the pressure were taken the bombardment would stop. To avoid this, a tube containing charcoal cooled by liquid air is connected with A, and this absorbs the carbon dioxide and enough of the hydrogen to keep the vacuum in the cathode ray state. To see what new gases are given off in consequence of the bombardment, a photograph is taken while the connection between A and B is cut off. After this is finished, and when the bom-

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[1] Ann. chim. phys., [8] **18**, 569.

[2] Phil. Mag., **23**, 192.

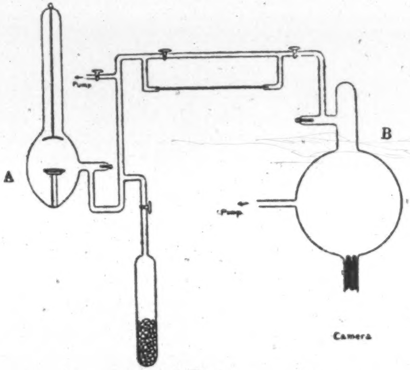
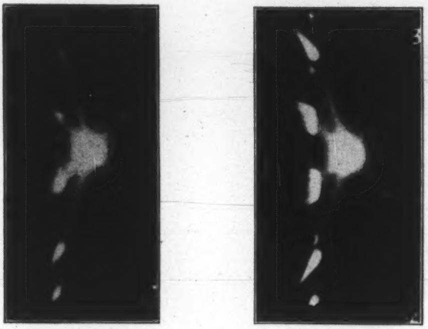


Fig. 4

bardment has gone on for about four hours, the tap is turned and a little of the gas from A is allowed to go into B; another photograph is taken, and those lines in the second photograph which are not in the first represent those gases which are liberated by the bombardment, and which have escaped being absorbed by the charcoal. I have here a slide (Fig. 5) representing the result of bombarding nickel. There are two photographs, one (α) before turning the tap and the other (β) after; in the second you see the three line very distinctly, while it is absent from the first, showing that the gas giving the three line has been liberated by the bombardment. I have got similar results to these when, instead of nickel, iron, copper, lead and zinc have been bombarded. I have tried two specimens of meteorites kindly lent to me from the Mineralogical Museum, Cambridge, and found there the three line. Nearly every substance I have tried gives, the first time it is bombarded, the helium line as well as this line due to X_3; if, however, the same substance is bombarded a second time, the helium line is in general absent (occasionally it is still to be detected, though exceedingly faint); and on the third bombardment is invisible in all the substances I have tried except monazite sand, where it is given off in exceedingly large quantities as long as the bombardment continues. It is remarkable that monazite sand, which contains so many elements, gives no trace of the three line when bombarded.

I have also obtained the X_3 line and also the helium line when the tube A was replaced by one containing a Wehnelt cathode; with this the current of cathode rays through the tube was much larger than with the other cathode, though the velocity of the rays was smaller. The Wehnelt cathode gives the line without placing pieces of metal in the tube, so that in this case nothing is bombarded by the cathode rays but the glass walls of the tube; the strip of metal forming the cathode is, however, bombarded by the positive rays.

The three line, when present at all, continues even though the bombardment is very prolonged. In some cases the bombardment has been prolonged for twenty hours, and at the end of that time the line seemed almost as bright as at the beginning; indeed, I could not feel certain that there was any difference. This might lead one to suspect that X_3 was manufactured from the lead or other metal by the bombardment rather than stored up in it, and this view might be regarded as receiving some support from the fact that very little of the X_3 is liberated by heating. The following experiment is an illustration of this: I took a piece of lead, and instead of bombarding it with cathode rays I placed it in a quartz tube connected



α **Fig. 5** *β*

with the vessel A, and heated the tube to a bright red heat for several hours. Large quantities of carbon dioxide and hydrogen were driven off by this process; this was absorbed by charcoal, and the residual gases, which had accumulated in A, were admitted into the vessel B; the X_3 line and helium line could just be detected, and that was all. I then gave the lead a second heating, raising this time the temperature until the quartz was on the point of softening. The lead was boiled vigorously; the heating was kept up for about three hours. In this time about three-quarters of the lead had boiled away. I then let the gases which had been given off at the second heating into the vessel B, and took another photograph; no trace of the line due to X_3 or helium could be detected. The fraction of the lead which had not been boiled away was now placed in A and bombarded by cathode rays. It now gave the three line quite distinctly; the helium line was visible, but faint. By the bombardment with the cathode rays the lead was only just melted, so that the average temperature was much less than when it was heated in the quartz tube. This rather suggests that the X_3 might be due to a kind of dissociation of the metal by the cathode rays, and not to a liberation of a store of that substance. Another experiment shows, however, that for lead, at any rate, this view is not tenable. I took some lead which had just been deposited from a solution of lead acetate by putting a piece of zinc into the solution, and forming the well-known lead tree. When I bombarded this freshly precipitated lead, I could get no trace of X_3 line; the helium line, too, was absent. I then tried another experiment. I took a piece of lead and divided it into two parts. The first of these I bombarded by the cathode rays: it gave the X_3 line quite distinctly. The other part I dissolved in boiling nitric acid, getting lead nitrate. The nitrate was heated and converted into oxide, and this was bombarded by the cathode rays: it did not give the X_3 line, showing that the X_3 is not produced by the bombardment, but is something stored up in the lead, which can be detached from it when the lead is dissolved. I have tried several samples of lead; the one which gave the X_3 line most distinctly was a piece of lead from the roof of Trinity College Chapel, several hundred years old. A sample of Kahlbaum's chemically pure lead, which must, I suppose, at no distant date have been subjected to severe ordeals by fire and water, showed the line quite distinctly, though not so well as the older lead. I have tried similar experiments with iron, and found that iron which gave the three line very distinctly ceased to do so after it had been dissolved in acid.

As the most obvious explanation of X_3 is that it is H_3, bearing the same relation to hydrogen that ozone does to oxygen, and produced in some way from the hydrogen dissolved in the metal, I tried if I could produce it by charging metals with large quantities of hydrogen, and then seeing if the hydrogen coming from the metal gave any traces of H_3. Thus, for example, I tested the hydrogen given off from hot palladium, but found no trace of X_3. I then charged nickel at a temperature of about 355° with hydrogen in the way recommended by Sabatier, but found no increase in the brightness of the X_3 over nickel that had not been deliberately exposed to hydrogen. I tried if the brightness of the line would be increased by adding hydrogen to the bulb A, in which the bombardment took place, but found no effect. I also tried adding oxygen to this bulb, thinking that if it was H_3 it would combine with the oxygen, and thus be eliminated, but no great diminution in the intensity was produced by this treatment. The gas seems quite stable, at least it can be kept for several days without suffering any diminution that can be detected; indeed, when once it has got into a bulb, there is considerable difficulty in getting the bulb free from it. It must be remembered, too, that by the method it is produced the gas is subjected all the time to electric discharges which would break it up unless it possesses very great stability. Thus if X_3 is a polymeric modification of hydrogen, it must possess the following properties:

1. It must be very stable
2. It must resist the action of oxygen
3. It must not be decomposed by long-continued exposure to the electric discharge.

These are properties which *a priori* we should hardly have expected an allotropic modification of hydrogen to possess.

Mendeléeff predicted the existence of an element with an atomic weight 3. According to him this element should be intensely electronegative and possess the properties of fluorine to an exaggerated extent. The gas X_3 can, however, be kept in glass vessels, which we should not expect to be possible if it possessed more than fluorine's power of combining with glass. I prefer to defer expressing any opinion as to the actual nature of the gas until I have had the opportunity of making further experiments upon it. It is only about two months ago that I found how to get the gas with any certainty, and, as the method involves long bombardments, each experiment takes a considerable time. This has prevented me from making several experiments which suggest themselves, and which ought to be made before coming to a final decision. I thought, however, that the investigation, though incomplete, might not be unsuitable for a Friday evening discourse, as the gas, whatever its nature, is certainly one of considerable interest, and its detection illustrates the delicacy of this new method.

SIR J. J. THOMSON

OBITUARY

LOUIS HENRY[1]

Louis Henry, the famous Belgian chemist, died at Löwen on March 9th, as the result of an apoplect c stroke which he suffered some two years earlier. He was more than 78 years old, having been born at Marche, Ardennes, on December 26, 1834. His father, an official in the Treasury Department, was frequently transferred, so that young Henry received his preparatory education in various schools. In 1851 he entered the University of Löwen and there obtained the doctor's degree in the natural sciences. After a brief stay at the University of Lüttich, with de Koninck, he went to Giessen to study under Will, the successor of Liebig. In 1858 he returned to Löwen to take charge of the Department of Mineralogy, and on the death of Prof. Marten a few years later succeeded him in the chair of Chemistry, which he retained until the beginning of his illness. In 1865 he was elected a corresponding member of the Belgian Academy of Sciences and in 1899 was awarded its prize for the most distinguished services to chemistry and physics.

Henry's name at once recalls his proof of the equivalence of the four valences of carbon. Designating the four valences by α, β, γ and δ, respectively, he prepared nitromethane, $CH_3.NO_2(\alpha)$, from silver nitrite and methyl iodide, and acetonitrile, $CH_3.CN(\alpha)$, from potassium cyanide and methyl iodide; this nitrile he hydrolyzed to acetic acid, $CH_3.COOH(\alpha)$, converted the latter into chloroacetic acid, $CH_2Cl.COOH(\alpha)$, and from this compound by the action of potassium nitrite he obtained a second nitromethane, $CH_3.NO_2(\beta)$. Again, the chloro acid, $(\beta)ClCH_2.COOH(\alpha)$, was converted into malonic acid, $CH_2(COOH)_2(\alpha,\beta)$, which, through the ethyl ester, was transformed into chloromalonic acid, $(\gamma)ClCH(COOH)_2(\alpha,\beta)$; this acid, on heating, yielded chloroacetic acid, $(\gamma)ClCH_2$-$COOH(\alpha \text{ or } \beta)$, which, with potassium nitrite, gave a third nitromethane, $CH_3.NO_2(\gamma)$. Finally, triethyl methanetricarboxylate, $CH(COOH)_3(\alpha,\beta,\gamma)$, obtained from the chloro acid, $(\gamma)ClCH(COOH)_2(\alpha,\beta)$, through the nitrile, gave the acid $(\delta)ClC(COOH)_3(\alpha,\beta,\gamma)$, and from this was obtained a fourth nitromethane, $CH_3.NO_2(\delta)$. Inasmuch as the four nitromethanes obtained by these methods were identical, Henry believed that the equivalence of the four valences of carbon was proved. Underlying this "proof," however, is, of course, the assumption that no migration of the atoms or groups occurs during the various reactions.

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[1] This sketch is based on a note by C. Aschman, Chem. Ztg., 37, 765 (1913).

Henry's discovery of dipropargyl, an isomer of benzene, also attracted the widest attention, on account of its bearing on Kekulé's theories.

REVIEWS

Literatur-Register der organischen Chemie, geordnet nach M. M. Richters Formelsystem. Herausgegeben von der Deutschen Chemischen Gesellschaft, redigiert von Robert Stelzner. Erster Band, umfassend die Literaturjahre 1910 und 1911, anschliessend an die dritte Auflage von Richters Lexikon der Kohlenstoff-Verbindungen. Braunschweig: Verlag von Friedrich Vieweg und Sohn. 1913. S. xxxix + 1286. Preis: geh., M. 84; geb., M. 86.

After the preparation of the third edition of his *Lexikon*, covering all the literature abstracted in the *Chemisches Zentralblatt* up to January 1, 1910, and including some 145,000 compounds, M. M. Richter announced to the Deutsche Chemische Gesellschaft that no one man was longer able to keep up with the ever-increasing flood of literature and that he would be compelled to give up the continuation of his work. The Society then took up the matter and sent out some 4000–5000 circular letters to members and nonmembers, asking their opinion as to the feasibility of publishing a biennial continuation of the *Lexikon* under the auspices of the Society, and whether they would be willing to subscribe for such a work. The response was very encouraging, but the number of subscriptions was not large enough to justify the undertaking, especially as the Society's resources were to be heavily taxed during the next few years by the forthcoming publication of the fourth edition of *Beilstein*. At this stage, with that spirit of coöperation so characteristic of German chemical manufacturers, the firm of Leopold Cassella & Co., Frankfurt am Main, contributed 60,000 marks, to be paid in three yearly installments, and as the result we have the present volume before us.

The work involved in the preparation of this book is truly appalling. The editor is Dr. Robert Stelzner, who, since 1897, has prepared the annual index of the *Berichte* and is thus peculiarly qualified for this kind of work. The compounds are arranged according to their empirical formulas as in Richter's *Lexikon*, but the present book is much fuller than the

Lexikon, especially as regards the more common compounds which, in the *Lexikon*, are designated as "Verbindungen mit bedeutender Literatur," with a single reference to *Beilstein*. In this *Literatur-Register*, on the contrary, after every compound treated are given the melting, solidifying, decomposition and boiling points (if newly determined within the period under consideration), then the references with as much text as will serve to briefly characterize the material content of the article referred to. These references are divided into the following groups: I. *Constitution and Configuration*. II. *Occurrence* (isolation, detection), *Preparation* (purification), *Methods of Formation*. III. *Physical Properties* and *Reactions* (influence on the properties of other substances) (*a*) of the substance itself and (*b*) when mixed with other substances: (1) Solidification, melting, decomposition and boiling points; 2. Molecular weight, cryoscopic and ebullioscopic behavior; 3. Density, expansion coefficient and other constants in the field of mechanics; 4. Optical behavior; 5. Thermochemical behavior; 6. Magnetochemical behavior; 7. Electrochemical behavior; 8. Solubility, behavior as solvent, partition between solvents. IV. *Chemical Behavior* (reactions, transformations) (*a*) towards inorganic substances, (*b*) towards organic compounds. V. *Physiological Behavior*. VI. *Determination* (analysis, separation). VII. *Use and Applications*. VIII. *Salts, Esters, Compounds with Other Substances*. As a single example of the magnitude of the work, it may be stated that under Acetic Acid are given some 425 references (not including the methyl and ethyl esters). In all, about 22,000 compounds are listed, with nearly 60,000 references. And this covers only two years!

From 22 of the more important journals and the *Deutsche Reichs-Patente*, the references have been prepared from the original articles and the corresponding *Chemisches Zentralblatt* reference added; for all other journals, the *Zentralblatt* has been followed.

The system of nomenclature used is a modified form of Richter's; the difficulties encountered by the editor in this connection again draw attention to our crying need for some uniform system. Dr. Stelzner also justly deplores the custom of publishing the same articles in more than one journal, and, which is even more serious, the carelessness of some authors in checking up formulas in reading proof and their failure, often, to indicate clearly what compounds they are working with. To quote from the Introduction: "We note with astonishment, for example, that some physical constant for 'xylene' is given to many places of decimals without the author indicating whether it is *o*-, *m*- or *p*-xylene. These cases gradually accumulated to such an extent in the course of the work that the editor, for lack of time, finally had to give up the attempt to clear up the matter by an inquiry to the author—especially as this attempt was often found to fail because the result of the inquiry brought only the admission that the author himself did not know with what isomer he had worked."

At the end of the volume is printed an alphabetical list of a large number of the common names of the substances treated in the body of the book, with their empirical formulas; structural formulas of the parent substances of the cyclic compounds; and such natural substances, biochemical products, etc., as have been dealt with during the period under review but which could not be incorporated in the *Register* because their composition is not known and which must therefore be looked up in the subject index of the *Zentralblatt*.

The book is indispensable in every organic laboratory and it is to be hoped that every chemist will coöperate with the editor and his staff in their tremendously difficult undertaking by complying in his publications with the three or four simple requests that they make; *viz.*, to check up all empirical and constitutional formulas, to indicate clearly the nature and position of all substituents in the compounds he is dealing with, and, in the case of stereoisomeric or optically isomeric compounds, whether they are *cis* or *trans*, dextro, levo, or racemic, and, when working with compounds of more or less uncertain composition, to point out either what is the more probably correct formula or that the composition is not yet established.

C. A. R.

TREATISE ON GENERAL AND INDUSTRIAL ORGANIC CHEMISTRY. By DR. ETTORE MOLINARI. Professor of Industrial Chemistry to the Society for the Encouragement of Arts and Manufactures and of Merceology at the Luigi Bocconi Commercial University, Milan. Translated from the second enlarged and revised Italian edition by THOMAS H. POPE, B.Sc., A.C.G.I., F.I.C., School of Malting and Brewing, University of Birmingham. With 506 illustrations. Philadelphia: P. Blakiston's Son & Co. 1913. pp. xix + 770. Price. $6.00.

The appearance of the first and second Italian editions of this unique book has already been noted in THIS JOURNAL.[1] English-speaking chemists will be sure to welcome the present translation. Mr. Pope has made a number of alterations and additions, consisting principally in amplifications of the statistical data referring to Great Britain and the United States. The translation reads smoothly and the work of the printer and binder has been well done.

C. A. R.

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[1] Vol. 44, p. 202; Vol. 49, p. 73.